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The Effect of Powered Activated Carbon in a Petroleum Refinery Activated Sludge Treatment System

Atlantic Richfield Co.
Harvey, IL

Prepared for

Robert S. Kerr Environmental Research Lab.
Ada, OK

Jun 82

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THE EFFECT OF POWDERED ACTIVATED CARBON IN A PETROLEUM REFINERY ACTIVATED SLUDGE TREATMENT SYSTEM

by

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Grant Number R804731-01

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16. ABSTRACT The purpose of this research program was to determine the effect of the addition of powdered activated carbon (PAC) to refinery activated sludge systems. Bench-scale and full-scale tests were performed. A wide range of PAC concentrations and sludge ages were evaluated.

Bench-scale activated sludge systems were designed and constructed. The bench-scale units were initially operated to determine the conditions of the full-scale test. Additional bench-scale tests were performed to evaluate conditions impractical to meet during the full-scale testing.

Similar results were obtained during the full-scale and bench-scale tests. A moderate enhancement of COD removal was observed. PAC addition had little effect upon the removal efficiency of other contaminants or the toxicity of undiluted effluents. An economic analysis of PAC addition was performed.

This report was submitted in fulfillment of Grant No. R804731-01 by the Atlantic Richfield Company under the sponsorship of the U.S. Environmental Protection Agency. This work covers the period January 1, 1977, to September 1, 1979, and work was completed as of September 1, 1979.

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the Nation's air, land and water resources can be assured, and the threat pollution poses to the welfare of the American people can be minimized.

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EPA's Office of Research and Development conducts this search through a nationwide network of research facilities. As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in ground water; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows; (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control, or abate pollution from the petroleum refining and petrochemical industries; and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

The use of activated carbon to improve the quality of discharge for an activated sludge wastewater treatment system has been considered by EPA as best-available-treatment technology for the petroleum refining industry. This report contains the findings of a study to determine the technical benefits and cost estimates of adding powdered activated carbon to a full-scale refinery activated sludge system.

Clinton W. Hall

Clinton W. Hall, Director
Robert S. Kerr Environmental
Research Laboratory

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ABSTRACT

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ABBREVIATIONS AND SYMBOLS

Abbreviations and Symbols - Text

BATEA	Best Available Technology Economically Available
BPT	Best Practicable Control Technology Currently Available
C	Concentration of TOC Remaining in Isotherm Test
COD	Chemical Oxygen Demand
DAF	Dissolved Air Flotation
DO	Dissolved Oxygen Concentration
F/M	Food to Mass Ratio
ft^2	Square Foot
GAC	Granular Activated Carbon
gpd	Gallons Per Day
gpd/ft^2	Gallons Per Day Per Square Foot
gpm	Gallons Per Minute
gpm/ft^2	Gallons Per Minute Per Square Foot
hp	Horsepower
k	Freundlich Constant
M	Quantity of PAC Used During Isotherm Test
MEA	Methyl Ethyl Amine
mg	Milligram
mg/1	Milligram Per Liter
ml	Milliliter
ml/min	Milliliter Per Minute
MLSS	Mixed Liquor Suspended Solida
MLVSS	Mixed Liquor Volatile Suspended Solids
n	Freundlich Constant
NH_3	Ammonia
P	Phosphorous
PAC	Powdered Activated Carbon
SA	Sludge Age
SVI	Sludge Volume Index
TOC	Total Organic Carbon
X	Quantity of TOC Removed During Isotherm Test

Abbreviations and Symbols - Appendix A

$\bar{d}$	Average Difference
k	Number of Experimental Treatments - Analysis of Variance
n	Number of Blocks - Analysis of Variance
	Number of Terms Making Each Mean - Multiple Range Test

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	Number of Data Pairs - Paired t-test
p	Number of Experimental Treatments - Multiple Range Test
S_B^2	Block Mean Square
S_R^2	Residual Mean Square
S_T^2	Treatment Mean Square
S_d	Standard Deviation of the Differences
S_m	Standard Error of the Means
S_B	Block Sum of Squares
S_T	Treatment Sum of Squares
S_R	Residual Sum of Square
$\bar{Y}$	Grand Average of Data Set
$\bar{Y}_i$	Average of $i^{\underline{th}}$ Block
$\bar{Y}_t$	Average of $t^{\underline{th}}$ Treatment
Y_{ti}	Observation sing the $t^{\underline{th}}$ Treatment in the $i^{\underline{th}}$ Block
β_i	Effect of the $i^{\underline{th}}$ Block
δ	Expected Difference
ε_{ti}	Error Associated With Observation
η	Mean of Data Set
σ^2	Variance of Residuals When Residuals Are Randomly Distributed With Mean Equal to Zero
τ_t	Effect of $t^{\underline{th}}$ Treatment

Abbreviations and Symbols - Appendix B

A	Fraction of Bio-Solids Remaining After HNO_3 Digestion
B	Fraction of PAC Remaining After HNO_3 Digestion
M	Concentration of PAC/Bio-Solids Mixture
M^1	Concentration of PAC/Bio-Solids Mixture After HNO_3 Digestion

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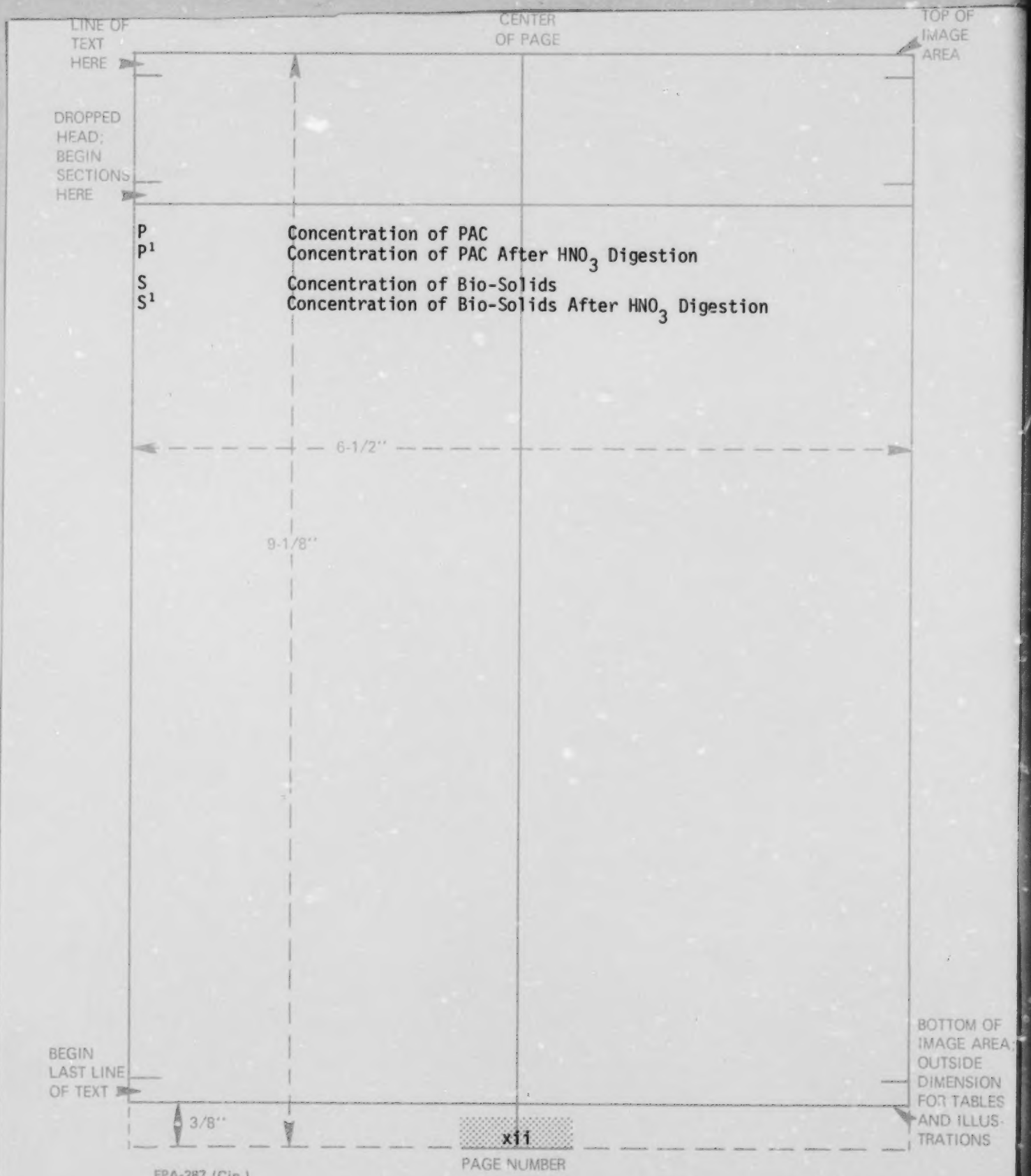

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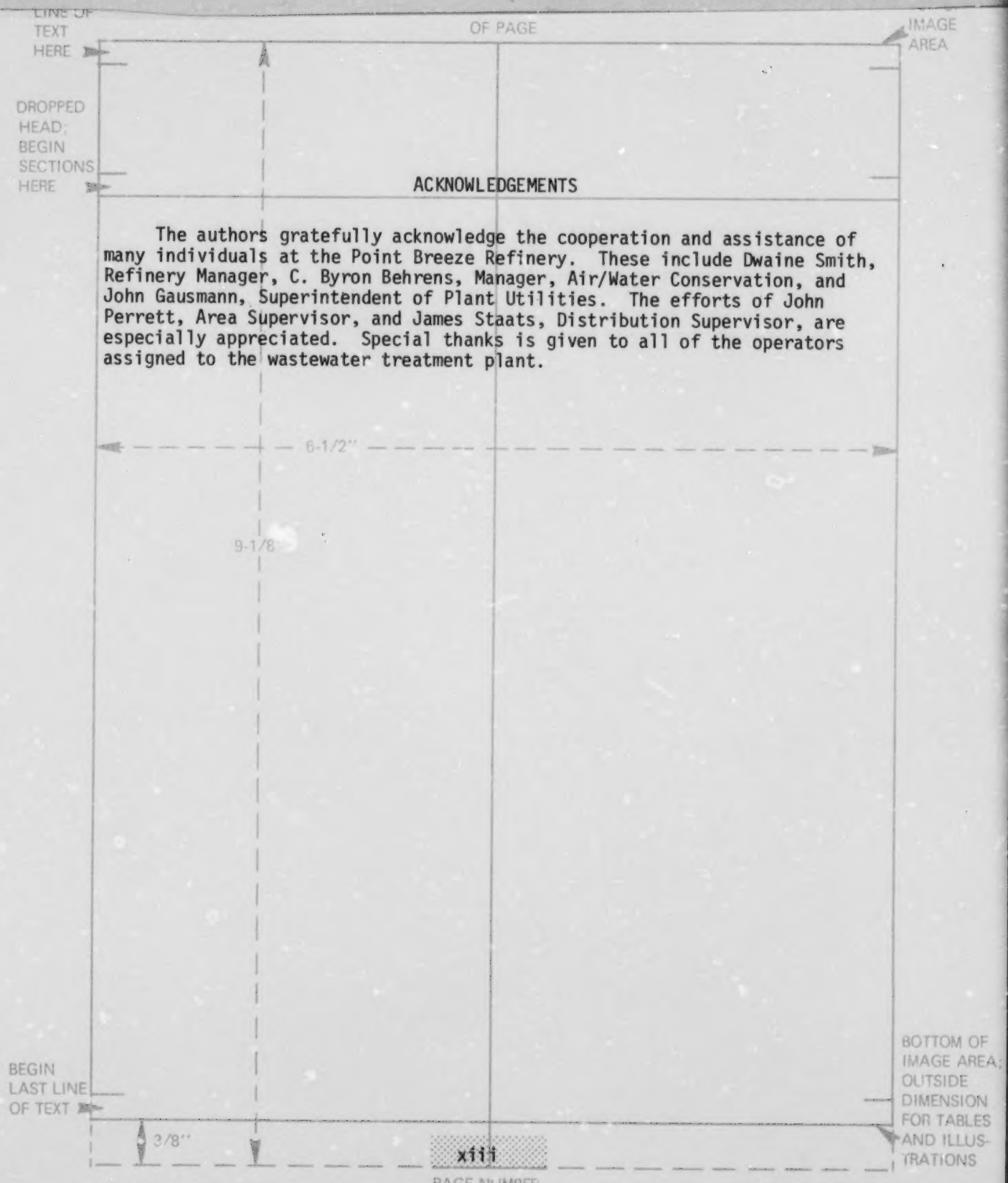

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SECTION 1

INTRODUCTION

The 1972 Water Pollution Control Act established a timetable for industry to adopt the "best practicable control technology currently available" (BPT) and the "best available technology economically achievable" (BATEA). The 1972 Act gave the Environmental Protection Agency (EPA) the authority to establish the technologies that constitute BPT and BATEA. In general, the refining industry has used biological treatment methods, such as activated sludge, to meet BPT effluent requirements. In the 1974 EPA draft guidelines for the Petroleum Refinery Point Source Category, the EPA established that BATEA be secondary treatment followed by granular activated carbon (GAC) treatment (1). Oil industry studies have shown that meeting the requirements of BATEA by adding GAC adsorption equipment to existing facilities would be an expensive step. The capital and operating costs of GAC adsorption and regeneration facilities may equal or exceed those of the entire current activated sludge process. Consequently, there has been considerable interest within the refining industry to develop cost-effective alternatives to GAC adsorption.

The addition of powdered activated carbon (PAC) to activated sludge is one alternative that has received considerable attention. The addition of PAC to activated sludge has the potential of improving system performance and effluent quality with a minimum capital investment. The purpose of the present study was to establish the effectiveness of the addition of commercially available PAC to refinery activated sludge systems meeting BPT requirements. Bench-scale and full-scale studies were performed. The main purpose of the bench-scale studies was to establish the conditions to be evaluated during the full-scale test. In addition, bench-scale reactors were operated at conditions that were impractical to meet during the full-scale testing.

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SECTION 2

CONCLUSIONS

1. The results from the bench-scale units were simiilar to those obtained from the full-scale units when operated under similar conditions.

2. PAC addition resulted in the moderate enhancement of chemical oxygen demand (COD) removal. During the bench-scale testing, the effluent COD from the PAC units was 11-33% less than from the control units. This corresponds to a 2-6% improvement in COD removal efficiency in the PAC units based upon the overall COD loading. During the refinery test, the effluent COD from the PAC unit was 18% less than from the control which corresponds to a 2% improvement in the overall removal efficiency of COD.

3. PAC addition resulted in a small, but statistically significant, enhancement of the removal of oil and grease. During the bench-scale tests the oil and grease in the effluents from the PAC units was 0.5-2.0 mg/1 less than in the control effluents. During the refinery test, the oil and grease concentration was 0.6 mg/1 less in the PAC effluent than in the control effluent.

4. PAC addition had little effect upon the removal efficiencies of TOC, total phenol, or total phosphorus.

5. PAC addition resulted in higher effluent suspended solids and ammonia concentrations during the refinery test.

6. PAC addition had little effect upon the removal of priority pollutants or the fish toxicity of the undiluted effluents during the refinery test.

7. PAC addition did result in increased sludge compactability and sludge settling rates.

8. PAC is abrasive and its use during the refinery test resulted in increased wear of sludge recycle pumps. It may be necessary to modify sludge handling equipment to prevent the adverse effects of abrasion when PAC addition programs are implemented.

9. The mixing requirements of PAC sludge are greater than conventional sludge. As was demonstrated during the refinery test, it may be ne-

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cessary to provide additional mixing to maintain the PAC sludge in suspension.

10. The mechanism of PAC enhancement appears to be simple adsorption. Biological regeneration of the PAC surface did not seem to occur.

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11. If the PAC addition program that was evaluated during the refinery test were implemented, the annual cost is estimated to be $603,500. This corresponds to a cost of $7.00/additional lb of COD removed and $104.95/additional lb of oil and grease removed.

12. In comparing the results of this study to results obtained in other recent refinery wastewater PAC studies, it becomes apparent that the effect of PAC addition depends upon the circumstances of the particular application. It should not be assumed that PAC addition will have a similar effect at all refineries. The suitability of PAC treatment should be tested in a bench-scale or pilot-scale study prior to adoption of a full-scale PAC program.

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SECTION 3

RECOMMENDATIONS

1. Since all refinery systems are not equally amenable to PAC treatment, future work should focus on what influent characteristics or operational factors control the effectiveness of PAC addition.

2. No evidence was found for the bio-regeneration of the PAC surface. Since other workers have claimed that bio-regeneration does ocur, future work should focus on the mechanism of PAC enhancement to determine under what conditions bio-regeneration occurs.

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SECTION 4

LITERATURE REVIEW

The process of PAC addition to activated sludge was developed and has been patented by E.I. DuPont de Nemours and Company (2). When PAC is added to activated sludge units, it is incorporated into the sludge matrix. Organics present in the wastewater are adsorbed onto the surface of the carbon. It has been postulated that microorganisms present in the sludge can utilize some of the absorbed organics. In this manner, the surface of the carbon may be "biologically regenerated." (3) Compounds that are not readily biodegradable within the normal retention time provided in an aeration basin, but are adsorbable, may thus be biologically degraded. PAC also acts as a weighting agent in the sludge; this results in increased settling rates and sludge compactability. Specific claims for the process include: 1) removal of refractory organics, 2) enhanced stability against shock loadings, 3) resistance to biologically toxic substances, 4) color removal, 5) foam suppression, and 6) improved sludge settling and dewatering characteristics. (4,5,6) DuPont has constructed and is operating a 40-MGD treatment plant at Deepwater, New Jersey which incorporates this technology.(7)

Several authors have reported the results of PAC addition to activated sludge systems in refineries. DeJohn and Adams have presented results of full-scale trials of PAC addition in four refinery and petrochemical plants.(8) They claimed that PAC addition resulted in improved organics removal, improved sludge settling, improved resistance to shock loadings, and improved color removal. Since these studies did not involve the use of a parallel control, it is difficult to draw conclusions from them. Rizzo has presented a case study of a full-scale trial of PAC addition at the Sun Oil Company refinery in Corpus Christi, Texas.(9) Results included improved solids settling, more uniform effluent quality, improved effluent quality, reduction in foaming, and fewer biological upsets. This study suffered from the same shortcoming as that of the studies reported by Adams and DeJohn: no parallel control.

Thibault et al. have published results from short-term bench-scale and full-scale tests of PAC addition.(10) Lignite-based and wood-based carbons were tested. Little improvement in system performance was observed at PAC concentrations less than 400 mg/1. Improvements in TOC and COD removal were observed at PAC concentrations of 1,000 - 2,000 mg/1. During the course of the testing, a shock loading of monethanol amine (MEA) was experienced. The performance of the PAC reactors deteriorated significantly during the upset. It was determined that a partial kill of the

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microbial population occurred in the PAC reactors but not in the control. This was attributed to the desorption of previously adsorbed materials in quantitites sufficient to be toxic to the biomass. It was concluded that PAC is most effective when used on a standby basis for low-cost treatment during shock loading. Another study by Thibault et al. involved the use of PAC concenrations of 2,000 mg/1 and 6,000 mg/1 at sludge ages of 20 and 60 days.(11) TOC and COD removals were both greater in the PAC units. The degree of improvement was greater in the PAC units with the 20-day sludge age. At the 20-day sludge age, the unit with the PAC concentration of 6,000 mg/1 performed slightly better than the 2,000-mg/1 unit. There was no difference between the 6,000-mg/1 PAC reactor and the 2,000-mg/1 PAC reactor at the longer sludge age. The most cost-effective enhancement was provided by the unit with the 60-day sludge age containing 2,000 mg/1 of PAC.

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Several other in-depth studies of the effect of PAC addition to activated sludge systems in refineries were performed simultaneously with the study reported here. Stenstrum and Grieves (12) and Grieves et al. (13) observed that PAC addition enhanced the performance of refinery activated sludge systems. They found that the degree of enhancement was affected by the surface area of the activated carbon. Best results were obtained with an experimental carbon characterized by an exceptionally high surface area, 2,500 m^2/g. This carbon is not commercially available. It was found that satisfactory performance could be obtained at low daily carbon makeup rates by maintaining a high sludge age. At a PAC concentration of 4,000 mg/1 and a 100-day sludge age, the PAC system approached the performance of activated sludge followed by GAC.

The American Petroleum Institute (API) has sponsored a two-phase study of PAC addition. These studies were similar to those of Grieves et al. and included the use of the high-surface-area experimental carbon. In Phase I, PAC concentrations of 500 - 2,500 mg/1 were used. (14) Enhancement of the activated sludge process was observed at PAC concentrations of 500-1,000 mg/1 with the experimental carbon. Enhancement was not observed in that concentration range with carbons commercially available. The degree of enhancement was greater when the carbon concentration was increased to 1,500 mg/1. The high-surface-area carbon dampened the effluent TOC perturbations during a MEA shock episode. The performance of the high-surface-area carbon at a PAC concentration of 2,500 mg/1 and a 50-day sludge age approached that of activated sludge followed by GAC treatment. The desorption of phenols from PAC and GAC was observed. An economic analysis suggested that the use of the high-surface-area carbon, a 50-day sludge age, and a PAC concentration of 2,500 mg/1 is a cost-effective alternative to GAC treatment.

Phase II of the API study was conducted at PAC concentratins of 2,500 mg/1 and 5,000 mg/1. (15) The high-surface-area experimental carbon again outperformed conventional carbon. Phenol removal at a PAC concentration of 5,000 mg/1 was comparable to removal by activated sludge followed by GAC treatment. However, with regard to TOC removal, treatment with GAC (average effluent TOC = 8 mg/1) outperformed the best PAC reactor (average

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effluent TOC = 18 mg/1). It was concluded that the mechanism for improved removal is mainly adsorption for TOC removal and adsorption followed by biodegradation for phenol removal.

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SECTION 5

BENCH-SCALE STUDIES

PROCEDURES

Treatment Scheme

Four bench-scale experimental programs were performed. In each program, four or five completely mixed activated sludge units were operated in parallel. Effluent from a refinery API separator was used as influent to the activated sludge reactors. Effluent from each secondary clarifier was filtered in a dual-media filter prior to discharge. The bench-scale treatment scheme is shown in Figure 1.

Process Wastewater

The bench-scale units were operated on API separator effluent obtained from a local Class B refinery. The wastewater was transported in 55-gallon polyethylene-lined drums. During summer months the drums were stored in a walk-in refrigerator at 1-3° C. In cold weather, the drums were stored outdoors. A 100-gallon refrigerated stainless steel tank was used for storage of the wastewater in the laboratory. Contents of the tank were mixed to provide a relatively uniform feed to the pilot units. The pH of each batch of wastewater was checked and adjusted to a pH of 7-7.5 with acid or base as required.

Sludge Wasting

Desired sludge ages were maintained by wasting a percentage of the solids under aeration each day. Solids lost in the effluent were credited toward this. It was assumed that the effluent suspended solids contained the same fraction of PAC as the mixed liquor suspended solids (MLSS). Sludges were wasted directly from the aeration vessel daily, Monday through Friday. The sludge was allowed to settle and the supernatant was returned to the reactor from which it originated.

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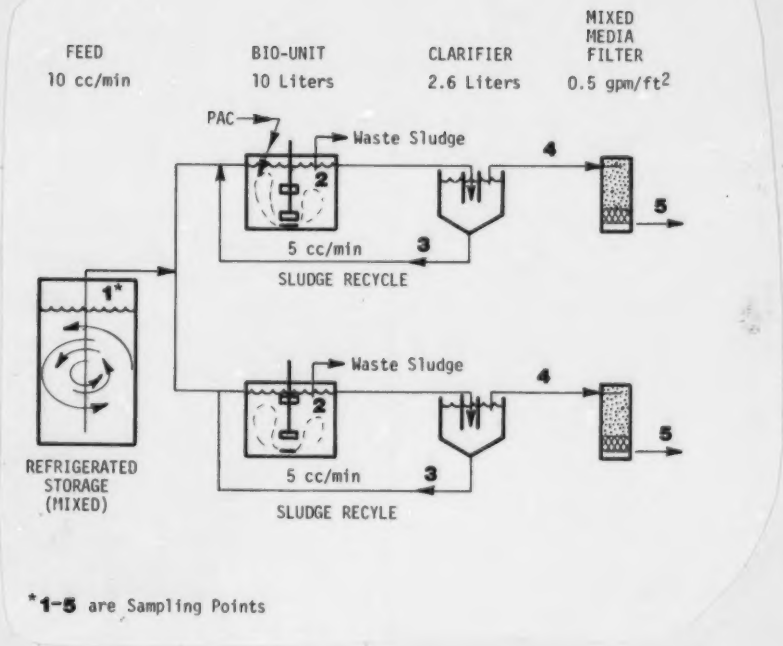

Figure 1. Bench-scale treatment scheme.

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Filter Backwash

The dual-media filters were backwashed daily, Monday through Friday. Deionized water was used to backwash the filters. Solids present in the filters were captured and allowed to settle. The settled sludge was returned to the reactor from which it originated. It was assumed that all of the solids in the filters were returned to the appropriate reactor. During Test Program 1, the backwashed solids were not returned to the reactors. This created operational problems which are described later.

Statistical Analysis

The data obtained in the bench-scale studies were analyzed statistically by a two-way analysis of variance (Appendix A). The daily feed concentration was used as the blocking variable. The analysis of variance is the standard statistical technique for comparing more than two experimental treatments. It is a technique for estimating how much of the toal variation in a set of data can be attributed to an assignable cause. The remainder, not attributable to an assignable cause, is classified as residual or error variation. The F-test indicates whether the assignable causes resulted in real variation or whether the variation is due to chance.

The F-test only indicates whether or not the variation in the data is significant. It does not indicate which of the experimental treatments differ. Duncan's Multiple Range Test was used to separate the treatment means (Appendix A).

The F-test is based upon the assumptions that the errors are independent, have constant variance and are normally distributed. In practice these assumptions can be approximated by randomly allocating the treatments to the experimental runs. (The t-test is based upon the same assumptions and randomization is also appropriate in that test.) Randomization insures that the experimental errors contribute homogeneously to the results for all the treatments. It was not physically possible to randomly assign the experimental treatments (i.e., presence or absence of PAC) to the activated sludge units each day. The experimental treatments were randomly assigned at the onset of each experimental program, however. At the start of the bench-scale program, the activated sludge units were operated under identical conditions and produced effluents which were not statistically distinguishable. Throughout the program, special care was taken to insure that the temperature, air flow, mixing rate, and feed rate were the same in all of the activated sludge reactors. Residuals obtained in analysis of variance were examined and found to be consistent. The results from all of the bench-scale studies were consistent.

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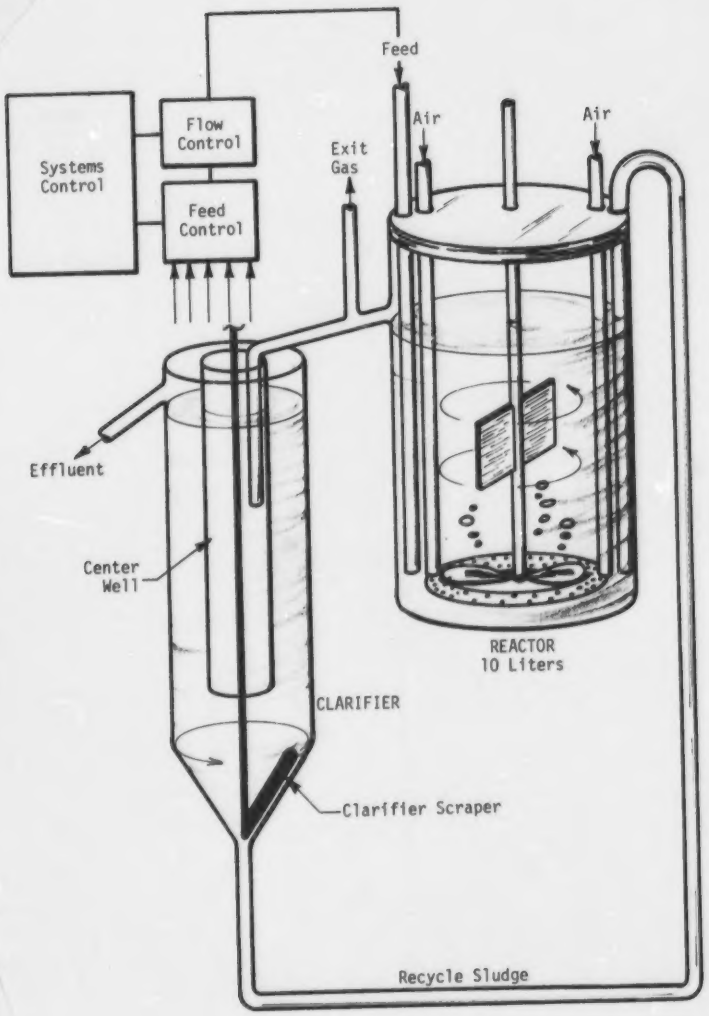

Figure 2. Bench-scale activated sludge unit.

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EQUIPMENT

Activated Sludge Units

Completely mixed activated sludge units consisted of 14-liter Pyrex glass reactors with stainless steel baffles and low sheer stirrers. An overflow tube was installed in the side of the container so that each reactor held 10 liters with the stirrers operating (Figure 2). API separator effluent was pumped into the reactors with Masterflex tubing pumps employing silicone rubber tubing. Flow was controlled at 10 ml/minute.

The dissolved oxygen (DO) level in each reactor was controlled at 1-2 mg/l and monitored continuously. The temperature was maintained at 32°C in the activated sludge reactors.

Overflow from the reactor entered the center wall of the glass clarifier. The overflow rate in the clarifier was 23.2 gpd/ft ^{2}.Sludge from the bottom of the clarifiers was recycled back to the reactors. The clarifier effluents entered the dual media filters and were pulled through the filters with tubing pumps. Filtered effluents were pumped to glass carboys which were stored at 1-2°C.

Dual Media Filters

Filter columns were fabricated from 1-inch ID Pyrex glass tubing with stainless steel end plates (Figure 3). The two end plates were held in place with four threaded rods running from one end to the other and fastened with wing nuts. Silicone rubber O-rings were used to seal the ends. Each filter was 40 inches in length with a 20-inch head space to handle fluctuations in flow and to prevent air from entering the filter bed. The filters were operated in a down-flow mode and backwashed manually as required. The hydraulic loading on each filter was 0.5 gpm/ft^2.

ANALYTIC PROCEDURES

Sampling

Daily, Monday through Friday, the entire flow through each dual media filter was collected in glass carboys. The carboy contents were maintained at a temperature of 1-2°C. One-half-gallon composite samples were obtained from each carboy daily. A daily influent composite sample was obtained by continuously sampling the influent line. The influent composite sample was also maintained at 1-2°C.

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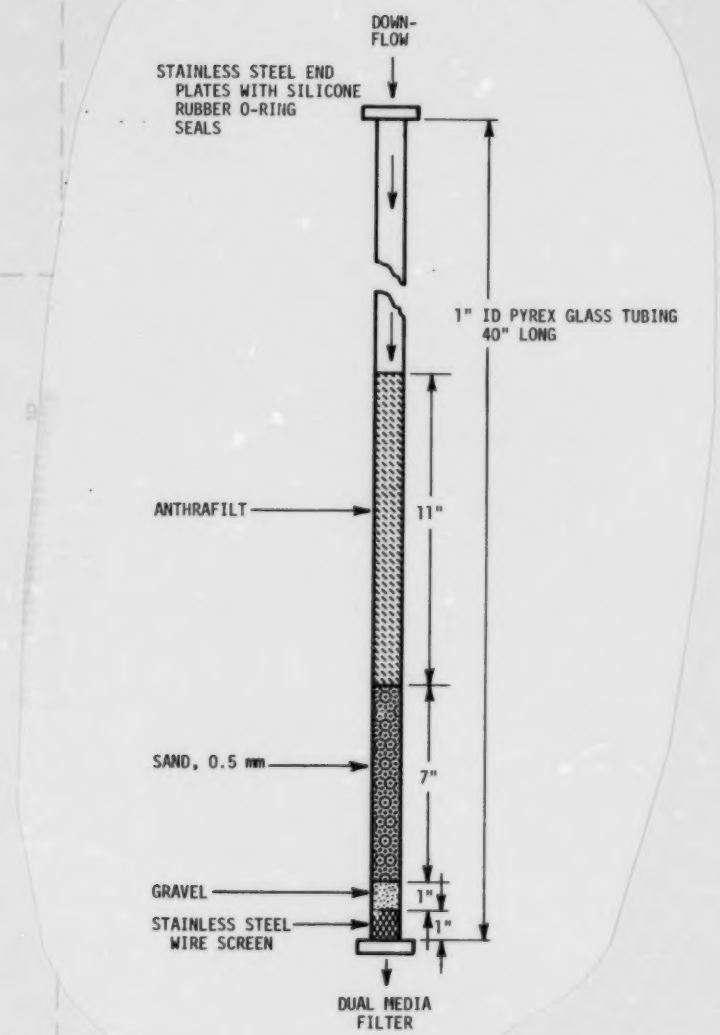

Figure 3. Bench-scale dual-media filter.

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Methods

Test methods for water quality analysis were generally selected from EPA approved methods (16). Oil and grease analysis was performed with an OCMA-200 oil content analyzer manufactured by Horiba Instruments. This instrument was chosen for its ease of operation and sensitivity in the low concentration range. Phenol analysis was performed using a simplified procedure supplied by the Hach Chemical Company. All analytic testing was performed in-house.

A method was devised to determine the PAC concentration in the MLSS. The method involves a nitric acid digestion of the sludges and is outlined in Appendix B. Oxygen uptake rates in the activated sludge reactors were measured in situ. The air flow to the reactors was increased until the DO in the reactors increased from the customary 1-2 g/1 to 5-6 mg/1. The air flow to the reactors was then stopped. The decay of DO concentration with time was monitored. Oxygen uptake rates are corrected for concentration of bio-solids and are reported as mg 0_2/g bio-solids/minute. Table 1 lists the sample points, collection frequencies, and testing program. The sampling points refer to Figure 1.

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TABLE 1. BENCH-SCALE SAMPLING AND ANALYTIC PROGRAMS

Sampling Point	Sample	Analysis	Frequency
1	24-hour Composite	pH	M-F
	24-Hour Composite	Oil and Grease, TOC COD, NH_3, Suspended Solids	M,W,F
	24-hour Composite	Phenol	T
	24-hour Composite	Total Phosphorous	Th
2	Grab	MLSS Concentration	M-F
	Grab	PAC Concentration	M, Th
	In Situ	DO, Temperature	Continuous
	In Situ	Oxygen Uptake	Occasionally
3	Grab	Recycle Sludge Concentration	Occasionally
4	Grab	TOC, Suspended Solids	Occasionally
5	24-hour Composite	pH	M-F
	24-hour Composite	Oil and Grease, TOC, COD, NH_3, Suspended Solids	M,W,F
	24-hour Composite	Phenol	T
	24-hour Composite	Total Phosphorous	Th

RESULTS

Powdered Activated Carbon Choice

The PAC was chosen from commercially available carbons on the basis of isotherm tests. PAC samples were obtained from Westvaco Corporation, ICI Americas, Inc., and Calgon Corporation. Isotherms were determined using the PAC samples and API separator effluent obtained at a local Class B refinery, dissolved air flotation effluent obtained from the ARCO Philadelphia refinery and secondary clarifier effluent obtained from the ARCO Philadelphia refinery and from the bench-scale units described earlier.

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Adsorption of organics on PAC is described by the Freundlich equation

$$\frac{x}{M} = kC^{1/n}$$

where: X = quantity of TOC removed (mg)
M = mass of carbon (mg)
C = TOC remaining (mg/1)

k and n = Freundlich constants.

The constants "n" and "k" define the nature of the carbon and adsorbate. A high "k" and "n" value indicates good adsorption throughout the concentration range. A low "k" and "n" value infers low adsorption at dilute concentrations and high adsorption at the more concentrated levels.

Isotherm tests were performed using four different carbons. Prior to testing, the carbon was dried at 103°C for 24 hours. After cooling, the carbon was weighed out into pint bottles and 300 ml of wastewater was added. The bottles were placed on a shaker table in a room maintained at 32°C. To ensure that equilibrium was reached, the samples were mixed for 24 hours on the shaker table. The samples were then filtered and analyzed for TOC.

Two of the carbons performed consistently better than the others with API separator effluent (Table 2). The two that performed poorly were discarded and further tests were performed using dissolved air flotation (DAF) effluent. Carbons 1 and 2 were also comparable with DAF effluent (Table 3). Isotherm tests were then run with carbons 1 and 2 and secondary clarifier effluent. Table 4 lists the average TOC removals at a PAC concentration of 2000 mg/1 for carbons 1 and 2. Because carbon 1 was comparable to carbon 2 with API separator and DAF effluents and was superior to carbon 2 with secondary clarifier effluent, carbon 1 was chosen as the PAC to be used in this test. Table 5 lists the properties of carbon 1.

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TABLE 2. ISOTHERM RESULTS - API SEPARATOR EFFLUENT

Carbon	PAC Concentration (mg/1)	Average % TOC Removal
1	500	28
	2000	50
2	500	25
	2000	48
3	500	11
	2000	31
4	500	9
	2000	28

TABLE 3. ISOTHERM RESULTS - DAF EFFLUENT

Carbon	PAC Concentration (mg/1)	Average % TOC Removal
1	500	30
	2000	68
2	500	29
	2000	69

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TABLE 4. ISOTHERM RESULTS - SECONDARY CLARIFIER EFFLUENT

Carbon	PAC Concentration (mg/1)	Average % TOC Removal
1	500	29
	2000	68
2	500	26
	2000	48

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TABLE 5. PROPERTIES OF PAC USED IN STUDY

Molasses Number	82
Iodine Number	950
Surface Area	519 m^2/g
Pore Volume Distribution	
<15A Radius	0.15 cm^3/g
15A-1000A Radius	0.36 cm^3/g
Total Radius	0.51 cm^3/g

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Preliminary Bench-Scale Studies

In order to establish that comparable results could be obtained from the bench-scale activated sludge units when operated under identical conditions, validation tests were conducted. Two reactors were operated for 76 days. The data were analyzed using the paired-t test. After startup and a two-week acclimation period, testing was performed while the reactors were operated under identical conditions. As shown in Table 6, the effluent quality from the two was similar and the results were statistically indistinquishable.

Additional tests were performed to establish the effect of DO concentration and variations in flow upon reactor performance. For a 3-week period, the DO in Reactor 1 was maintained in the range of 1.5 - 2.0 mg/1 while the DO in Reactor 2 ranged from 0.5 mg/1 - 1.0 mg/1. The results are shown in Table 7. The effluent suspended solids and COD were significantly less in Reactor 1. The reactors were also operated for a 2-week period with a varying flow rate while maintaining the DO differential. The flow was increased to 20 ml/minute for 8 hours each day in both reactors. During the remainder of the day the flow was maintained at 10 ml/minute. This reduced the hydraulic retention time in the aeration basins from 16.7 hours to 12.5 hours. As shown in Table 8 the effluent from Reactor 1 was considerably better than from Reactor 2.

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TABLE 6. PRELIMINARY BENCH-SCALE STUDIES - IDENTICAL CONDITIONS

Parameter	Reactor 1	Reactor 2	Significant at 95% confidence level
Suspended Solids (mg/1)	16.3	15.7	No
COD (mg/1)	57.8	58.7	No
NH_3 - N (mg/1)	0.6	0.8	No
Oil and Grease (mg/1)	5.0	4.8	No

TABLE 7. PRELIMINARY BENCH-SCALE STUDIES - VARYING DO

Parameter	Reactor 1	Reactor 2	Significant at 95% confidence level
Suspended Solids (mg/1)	23.8	40.3	Yes
COD (mg/1)	83.3	101.9	Yes
NH_3 - N (mg/1)	1.7	2.7	No
Oil and Grease (mg/1)	9.3	10.8	No
Dissolved Oxygen (mg/1)	1.5-2.0	0.5-1.0	

TABLE 8. PRELIMINARY BENCH-SCALE STUDIES - VARYING DO AND FLOW

Parameter	Reactor 1	Reactor 2	Significant at 95% confidence level
Suspended Solids (mg/1)	9.8	33.8	Yes
COD (mg/1)	43.5	89.1	Yes
NH_3 - N (mg/1)	3.2	3.8	No
Oil and Grease (mg/1)	3.8	6.1	Yes
Dissolved Oxygen (mg/1)	1.5-2.0	0.5-1.0	

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Test Program 1

The objective of this program was to determine the minimum PAC concentration that would significantly improve effluent quality over the control unit. Four laboratory-scale pilot units were operated in the following modes:

A. 2000 mg/1 Biosolids
B. 2000 mg/1 Biosolids + 500 mg/1 PAC
C. 2000 mg/1 Biosolids + 1000 mg/1 PAC
D. 2000 mg/1 Biosolids + 1500 mg/1 PAC

The four systems were operated continuously for a period of 9 weeks. It was intended that the daily PAC makeup rate be 3% (corresponding to a 33-day sludge age). However, uncontrolled carbon losses occurred in Reactors B and C. The PAC daily makeup rates were 7% in Reactor B (350 mg/day), 4% in Reactor C (400 mg/day), and 3% in Reactor D (450 mg/day).

The data are presented graphically in Figures 4-7 and are summarized in Table 9. The results for the three reactors which contain PAC are similar. Note that on average, there was a 40% reduction in oil and grease, 15% reduction in COD, and 12% reduction in TOC in the reactors with PAC as compared to the control. The effluent data presented are dual-media filter effluent.

The data were analyzed using the analysis of variance. The daily feed concentrations were used as a blockage variable. The results are shown in Table 10. There were significant differences in the oil and grease and COD results. Duncan's Multiple Range Test was performed on the oil and grease and COD data. There is no significant difference between the three reactors with PAC. There is a significant difference in COD and oil and grease between those three reactors and the control.

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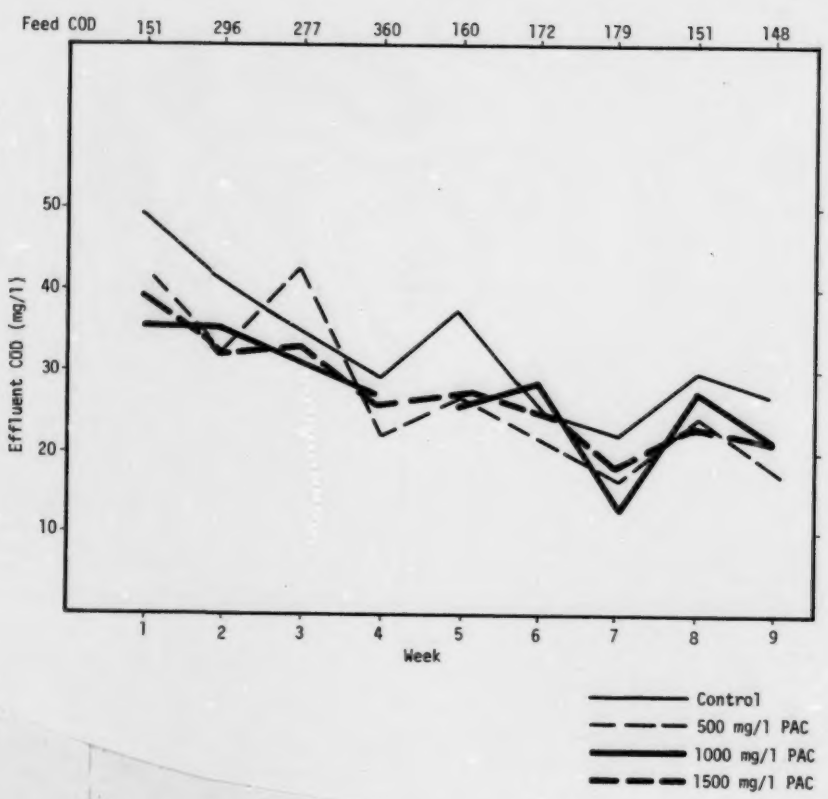

Figure 4. Test Program 1, weekly average chemical oxygen demand levels.

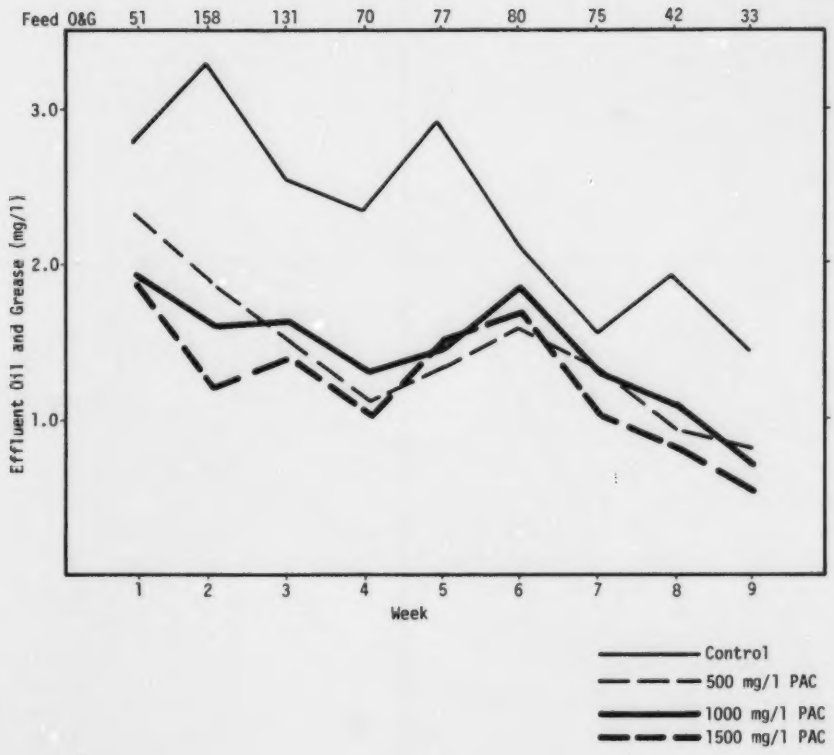

Figure 5. Test Program 1, weekly average oil and grease levels.

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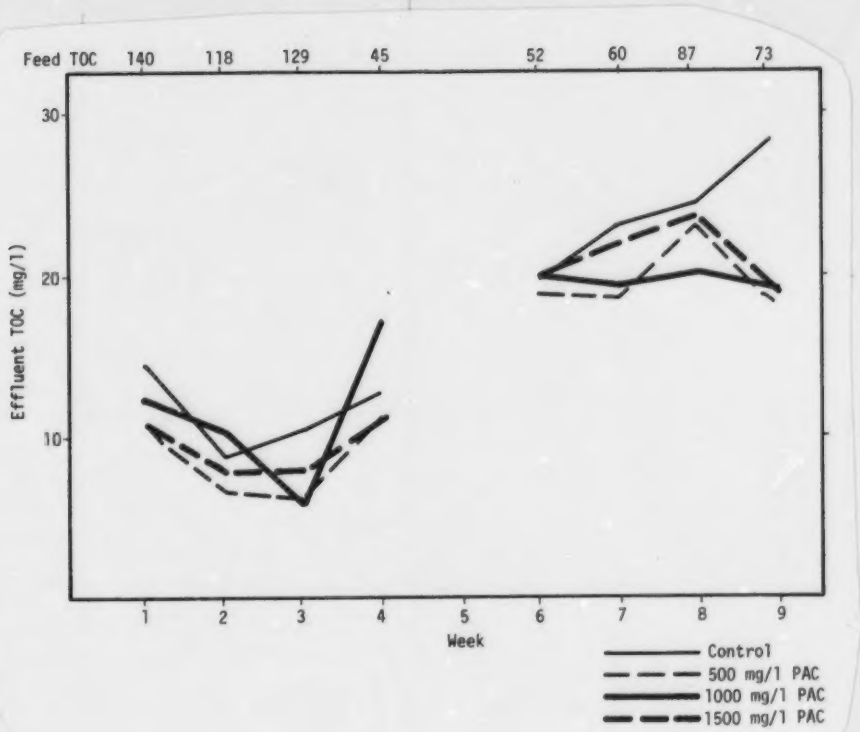

Figure 6. Test Program 1, weekly average total organic carbon levels.

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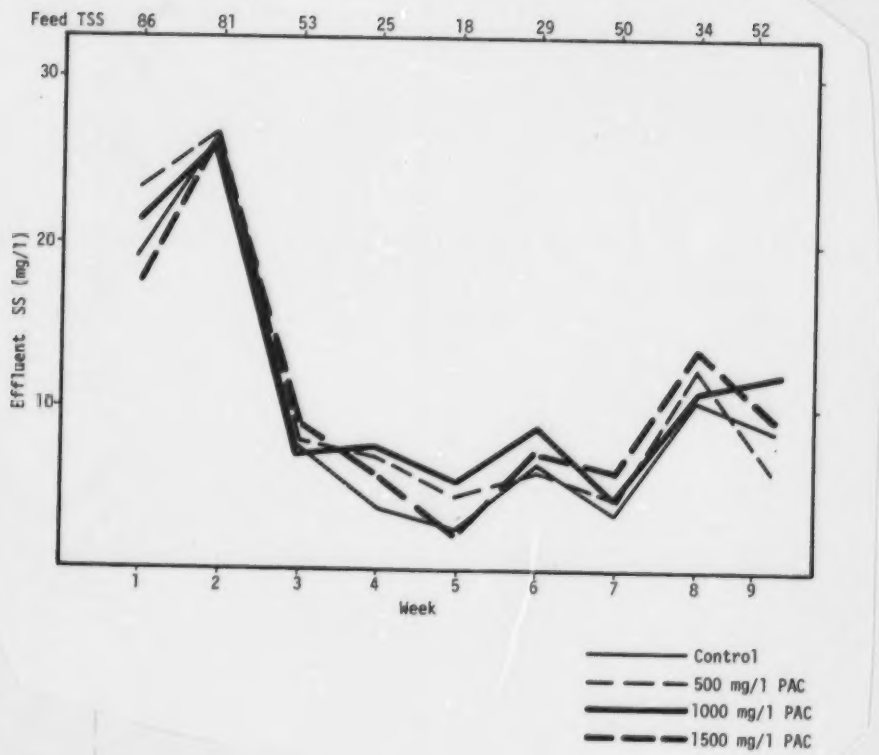

Figure 7. Test Program 1, weekly average total suspended solids levels.

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TABLE 9. SUMMARY OF RESULTS OF EFFLUENT QUALITY TESTS (AVERAGES, mg/1) -- TEST PROGRAM 1

Parameter	A	B	C	D
Bio-Solids	2000	2000	2000	2000
PAC	0	500	1000	1500
TOC	16.7	15.1	14.1	15.1
COD	33.3	27.8	28.3	28.2
NH_3 - N	0.04	0.09	0.04	0.03
Oil and Grease	2.4	1.5	1.4	1.3
Suspended Solids	9.7	10.6	10.8	11.2
Total P	0.2	0.2	0.1	0.1
Phenols	0.032	0.029	0.024	0.021
O_2 Uptake (mg O_2/mg Bio-Solids/minute)	.09	.08	.10	.07

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TABLE 10. SUMMARY OF STATISTICAL ANALYSIS -- TEST PROGRAM 1

Parameter	Calculated f-Value	Degrees of freedom	Significance level	Grouping
TOC	1.91	3.60	0.86	--
COD	5.40	3.69	>0.99	(A),(B,C,D)
NH_3 - N	0.901	3.48	0.55	--
Oil and Grease	31.14	3.69	>0.99	(A),(B,C,D)
Suspended Solids	1.2	3.66	0.69	--
Total P	2.07	3.23	0.86	--
Phenols	0.58	3.12	0.36	--
O_2 Uptake	0.40	3.28	0.24	--

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There was no difference in the performance of Reactors B,C, and D, despite the fact that the PAC concentration varied from 500 mg/1 - 1500 mg/1. However, because of uncontrolled carbon losses, the carbon makeup rates were similar in each reactor. Thus, it seems that it is not the PAC concentration but rather the PAC makeup rate which determines reactor performance.

Test Program 2

The objective of this program was to determine the effect of Food/Mass (F/M) ratio upon PAC reactor performance and to determine the effect of a higher PAC concentration. Four laboratory-scale pilot units were operated in the following modes:

A. 4000 mg/1 Biosolids
B. 4000 mg/1 Biosolids + 2000 mg/1 PAC
C. 2000 mg/1 Biosolids + 2000 mg/1 PAC
D. 2000 mg/1 Biosolids

In order to control solids losses in the PAC reactors, the backwash water was captured, as described in the Filter Backwash section. The solids were allowed to settle and the thickened solids were returned to the reactor from which they originated. In addition, before makeup carbon was added, it was wetted in 250 ml of solids-free mixed liquor. This supension was boiled for 5 minutes to insure thorough PAC wetting. This procedure made it possible to carefully control solids losses and was used throughout the remainder of the bench-scale studies. A makeup rate of 3% was used in Reactors B and C (33-day sludge age). A 33-day sludge age was also maintained in Reactors A and D.

Figures 8-11 are graphs of the results. The results are summarized in Table 11. Note that there was a 19% decrease in effluent COD in the low F/M PAC reactor and a 13% decrease in the high F/M reactor. The TOC results were worse for the two reactors which contained PAC. Oil and grease values were lower in Reactors B and C. The highest oil and grease concentrations were in the low F/M control.

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TABLE 11. SUMMARY OF RESULTS OF EFFLUENT QUALITY TESTS (AVERAGES, mg/1)
--
TEST PROGRAM 2

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Parameter	A	B	C	D
Bio-Solids	4000	4000	2000	2000
PAC	0	2000	2000	0
TOC	12.1	15.0	14.8	10.6
COD	53.8	43.7	43.4	50.0
NH_3 - N	1.6	0.8	0.3	0.4
Oil and Grease	2.3	1.6	1.2	1.7
Suspended Solids	14.3	13.9	15.1	12.6
Total P	0.5	0.7	0.5	0.6
pH	7.2	7.3	7.3	7.3
O_2 Uptake (mg O_2/mg Bio-Solids/min)	0.07	0.09	0.06	0.08

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TABLE 12. SUMMARY OF STATISTICAL ANALYSIS --TEST PROGRAM 2

Parameter	Calculated f-Value	Degrees of freedom	Significance level	Groupings
TOC	2.54	3.18	0.91	--
COD	5.54	3.66	0.99	(A,D),(B,C)
NH_3 - N	5.49	3.39	0.99	(A),(B,C,D)
Oil and Grease	11.02	3.69	0.99	(A),(B,C),(B,D)
Suspended Solids	1.49	3.81	0.78	--
Total P	6.97	3.21	0.99	(A,C,D),(B,D)
pH	69.0	3.87	0.99	(A),(B,C,D)
O_2 Uptake	0.52	3.22	0.32	--

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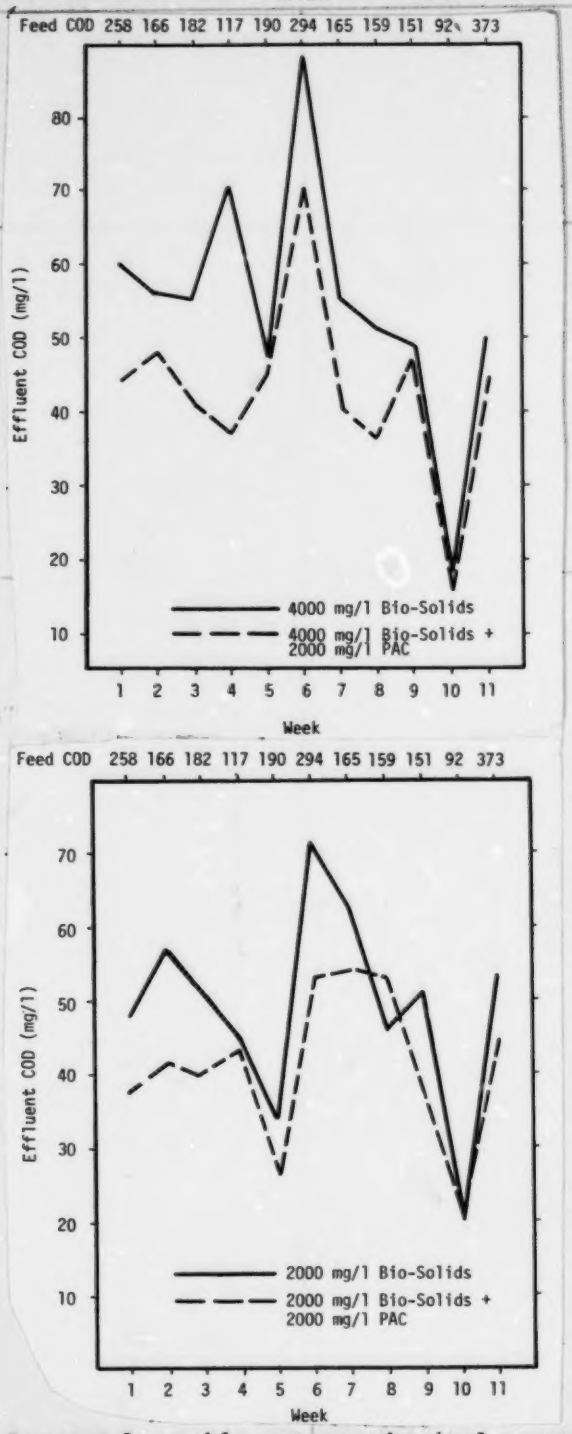

Figure 8. Test Program 2, weekly average chemical oxygen demand levels.

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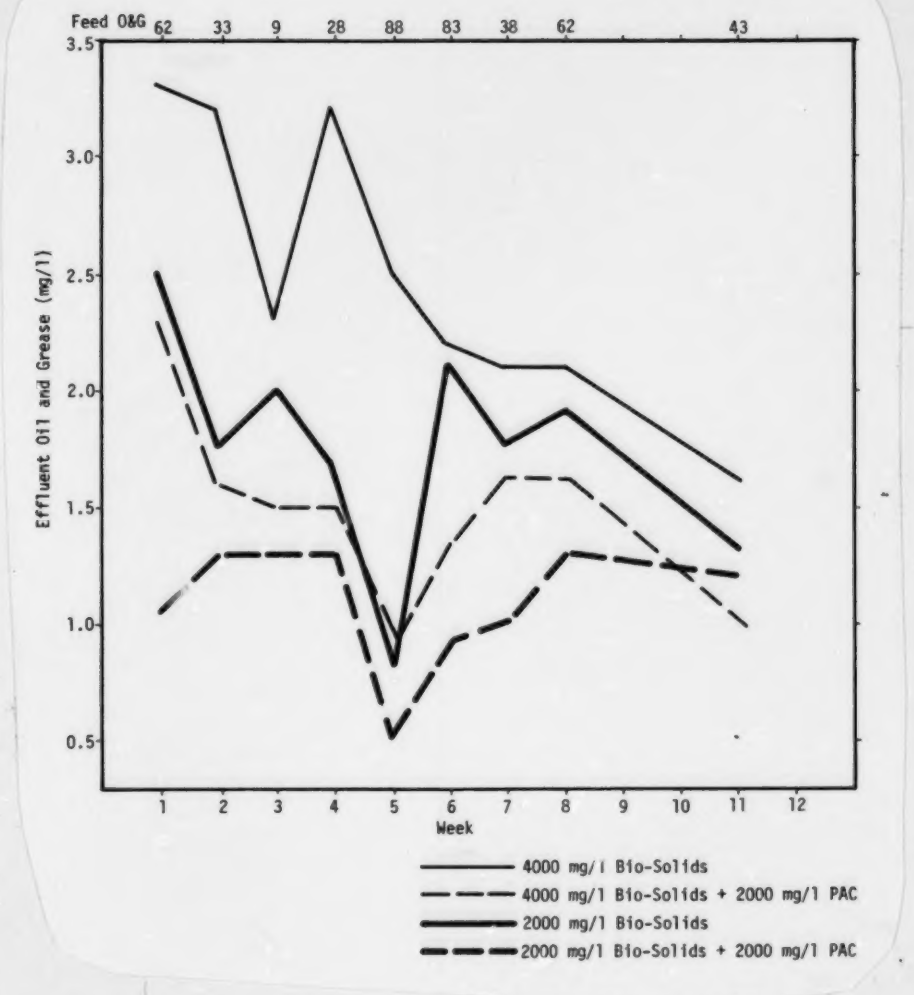

Figure 9. Test Program 2, weekly average oil and grease levels.

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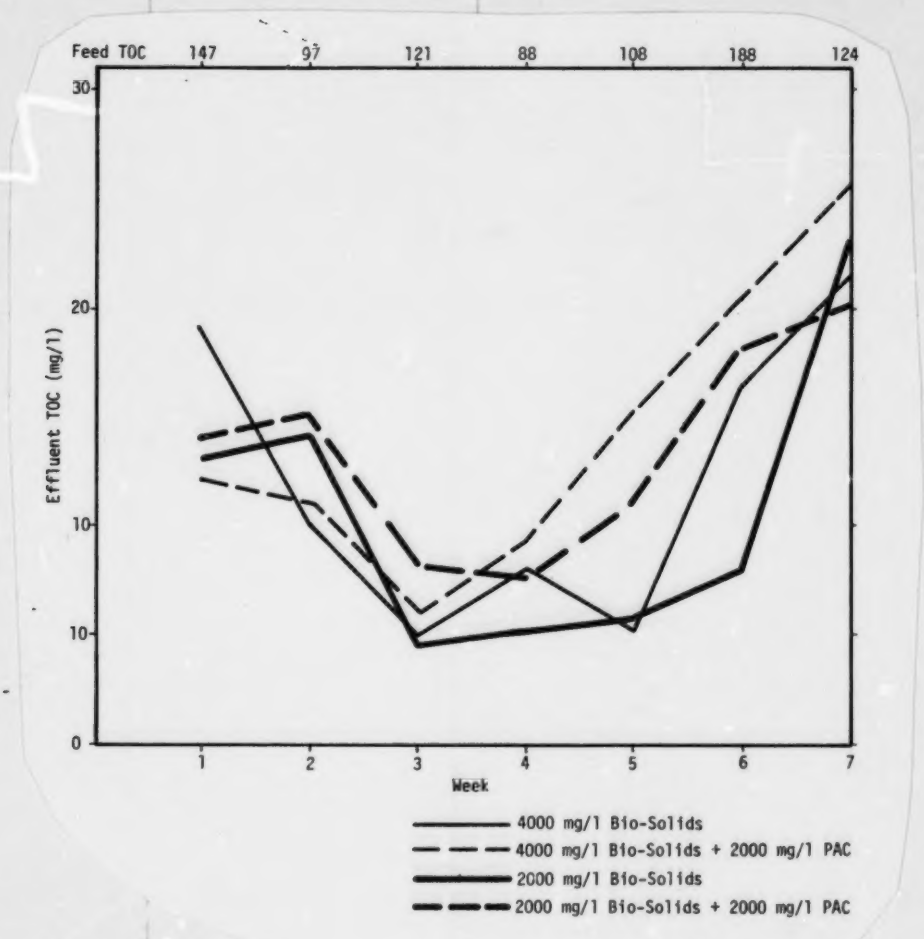

Figure 10. Test Program 2, weekly average total organic carbon levels.

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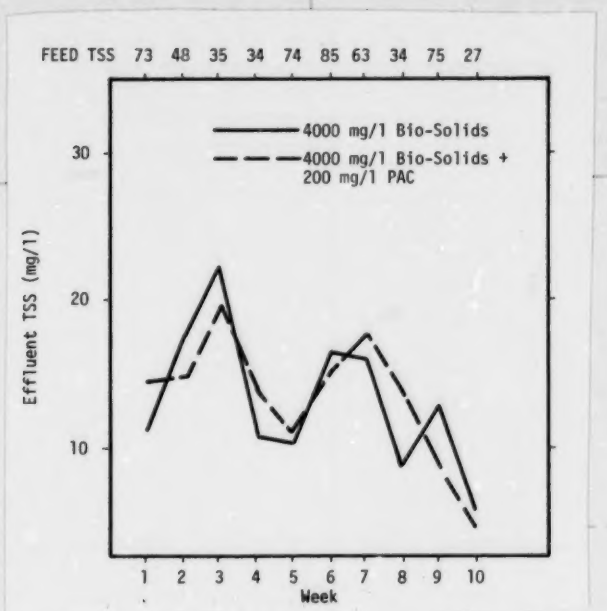
FEED TSS 73 48 35 34 74 85 63 34 75 27
4000 mg/l Bio-Solids
4000 mg/l Bio-Solids + 200 mg/l PAC
Effluent TSS (mg/l)
30
20
10
1 2 3 4 5 6 7 8 9 10
Week

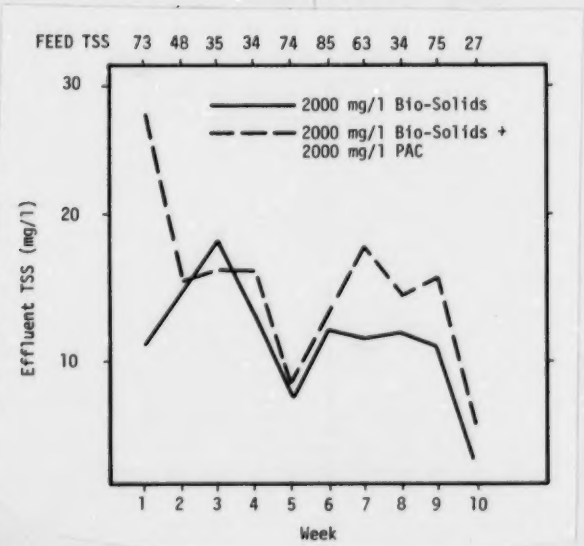
FEED TSS 73 48 35 34 74 85 63 34 75 27
2000 mg/l Bio-Solids
2000 mg/l Bio-Solids + 2000 mg/l PAC
Effluent TSS (mg/l)
30
20
10
1 2 3 4 5 6 7 8 9 10
Week

Figure 11. Test Program 2, weekly average total suspended solids levels.

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These data were analyzed using the analysis of variance with the daily feed concentrations as the blocking variable. Duncan's Multiple Range Test was performed on those sets of data showing significant differences. The results of the analysis of variance and Duncan's Test are shown in Table 12. It can be seen that with regard to COD reduction, there was no difference between the controls (A and D) or between the PAC reactors (B and C). The effluent COD was significantly less in the PAC reactors. There is no difference in the effluent oil and grease levels between the two PAC reactors. Note that the high F/M control was indistinguishable from the low F/M PAC reactor.

Test Program 3

The purpose of this test was to determine the effect of higher PAC concentrations at 30- and 60-day sludge ages. Five laboratory-scale pilot units were operated in the following modes:

A. Control, SA = 30 days
B. PAC = 2500 mg/1, SA = 60 days
C. PAC = 2500 mg/1, SA = 30 days
D. Control, SA = 60 days
E. PAC = 5000 mg/1, SA = 60 days

Other workers have claimed that high PAC concentrations at sludge ages greater than 30 days produces the greatest enhancement (12, 13). Note that the daily PAC makeup requirement is the same for Reactors E and C.

The averages for this test program are shown in Table 13 and the results of the statistical analysis are shown in Table 14. The data are shown in Figures 12-15. At a 60-day sludge age, the average effluent COD from the reactor with 2500 mg/1 PAC (Reactor B) was 10.6% less than the control. Operating at a PAC concentration of 5000 mg/1 resulted in 18.7% improvement in effluent COD. At the 30-day age, PAC addition of 2500 mg/1 resulted in 26.7% improvement in the effluent COD. The performance of Reactors C and E with regard to COD removal were statistically indistinguishable. The Reactors C and E were significantly better than Reactor B which had a PAC makeup rate one-half that of the others.

Oil and grease removals were improved in the three reactors which contained PAC. The three PAC reactors performed comparably with a 23.7% improvement with Reactor B, 21.1% improvement with Reactor E, and a 38.6% improvement in Reactor C. Suspended solids removal was slightly better in Reactor A than in the other reactors.

COD and oil and grease removals were significantly improved by the addition of PAC. PAC made the greatest improvement at the higher make-up rate. The effluent oil and grease concentrations were comparable in all three PAC reactors. The PAC makeup rate seems to be crucial to COD performance as Reactors C and E with a PAC makeup of 833 mg/day were indis-

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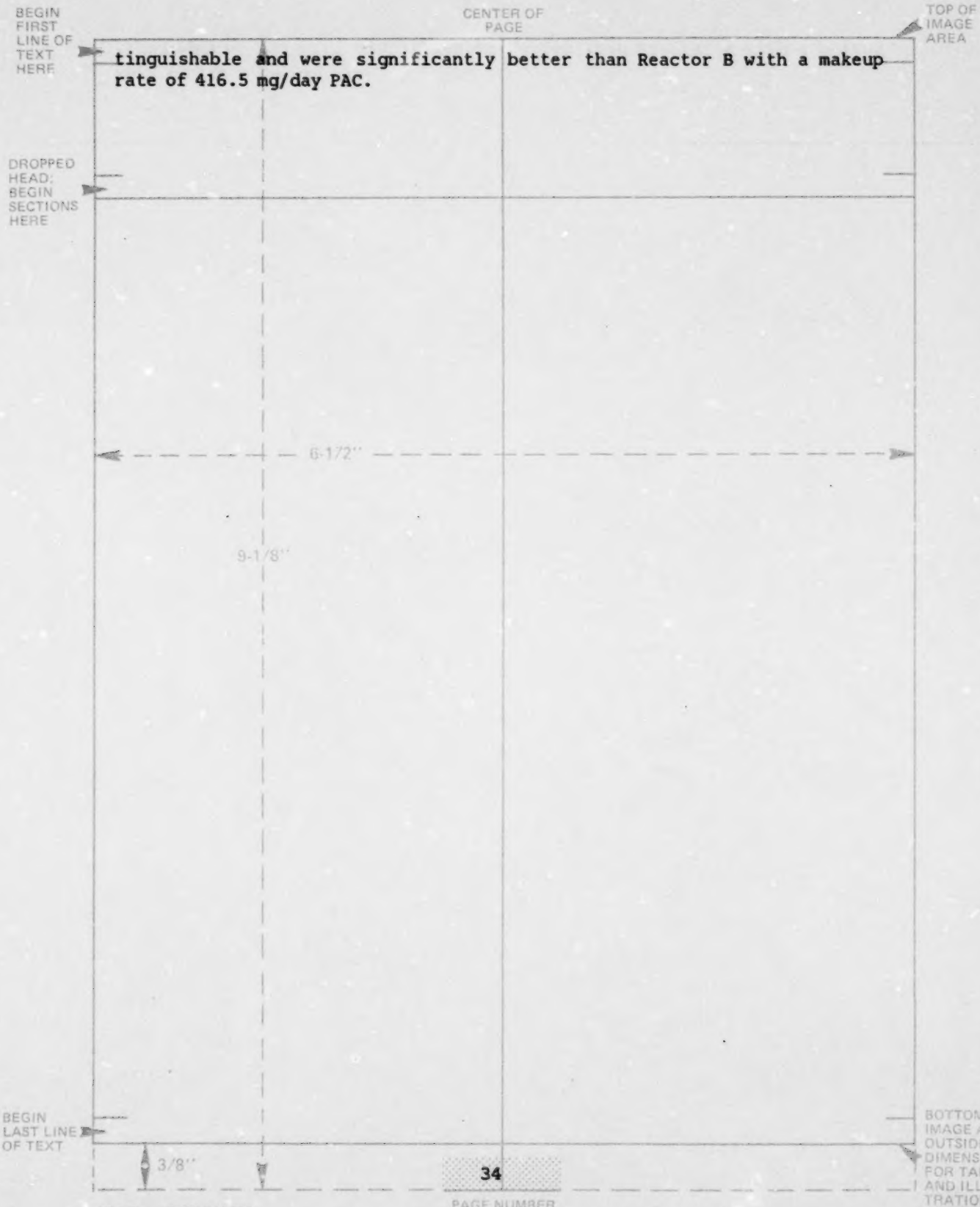
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tinguishable and were significantly better than Reactor B with a makeup rate of 416.5 mg/day PAC.
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TABLE 13. SUMMARY OF RESULTS OF EFFLUENT QUALITY TESTS (AVERAGES, mg/1)--TEST PROGRAM 3

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Parameter	A	B	C	D	E
Sludge Age (days)	30	60	30	60	60
Bio-Solids	2200	3100	2400	3000	3300
PAC	0	2500	2500	0	5000
PAC Addition Rate (mg/1)	0	417	833	0	833
TOC	26.2	23.9	24.1	27.1	25.1
COD	51.7	44.0	37.9	49.2	40.0
NH_3 - N	0.1	0.1	0.1	0.1	0.1
Oil and Grease	4.4	2.9	2.7	3.8	3.0
Suspended Solids	14.3	15.1	15.9	17.0	17.1

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TABLE 14. SUMMARY OF STATISTICAL ANALYSIS--TEST PROGRAM 3

Parameter	Calculated F-value	Degrees of freedom	Significance level	Groupings
TOC	0.82	4.13	0.46	--
COD	16.85	4.17	>0.99	(A,D),(B)(C,E)
NH_3 - N	1.96	4.11	0.83	--
Oil and Grease	11.94	4.11	>0.99	(A,D),(B,C,E)
Suspended Solids	14.3	4.11	>0.99	(A),(B,C,D,E)

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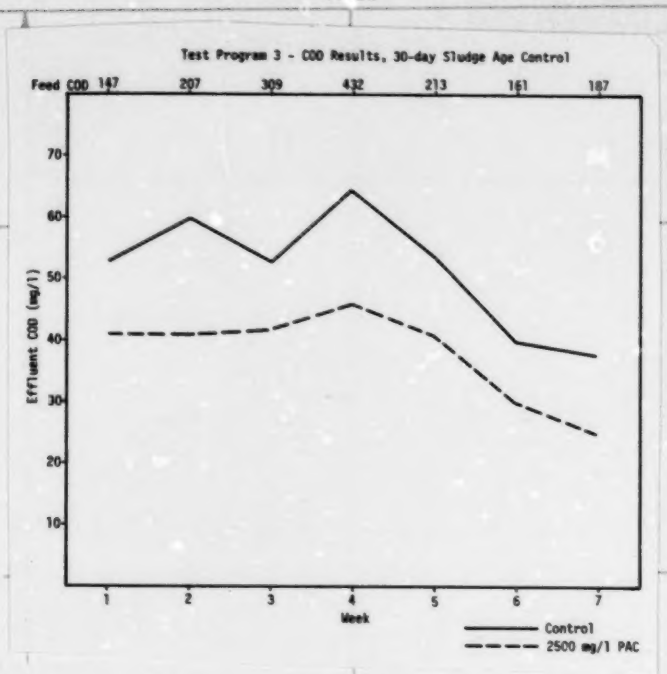

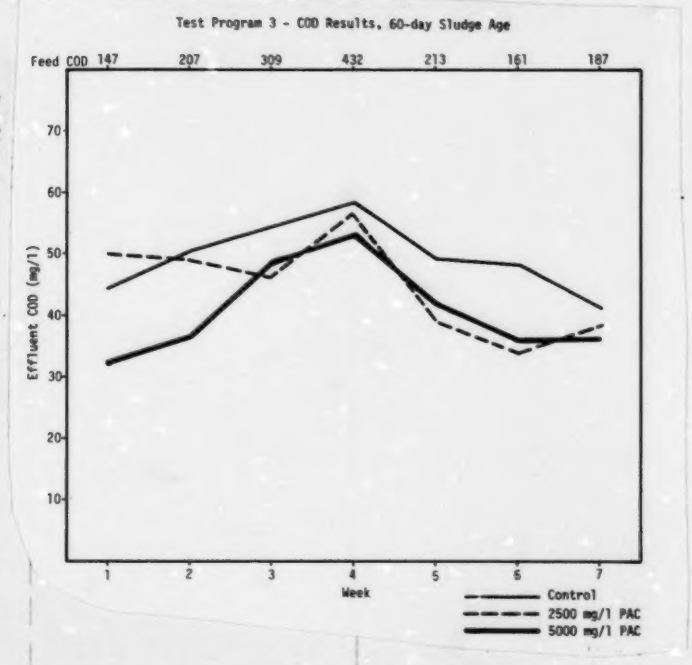

Figure 12. Test Program 3, weekly average chemical oxygen demand levels.

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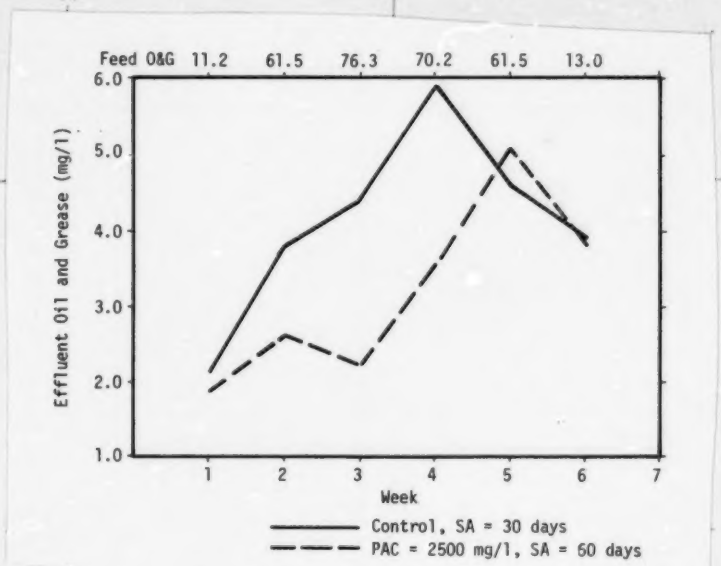

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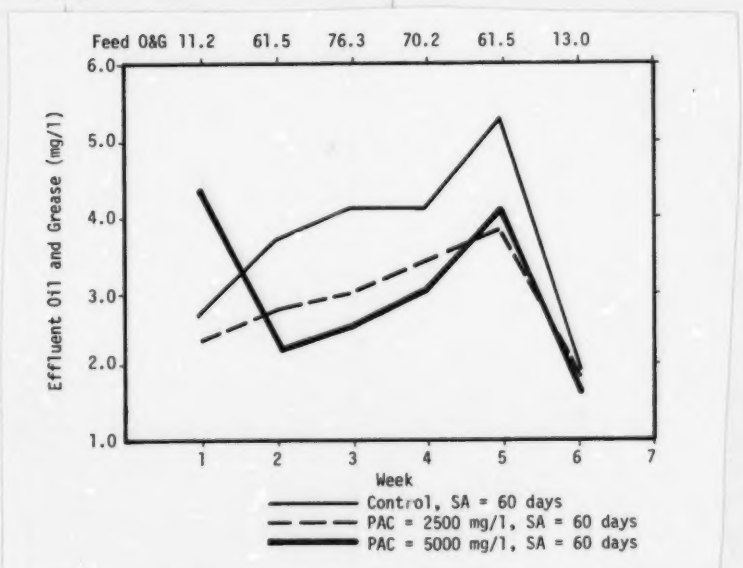

Figure 13. Test Program 3, weekly average oil and grease levels.

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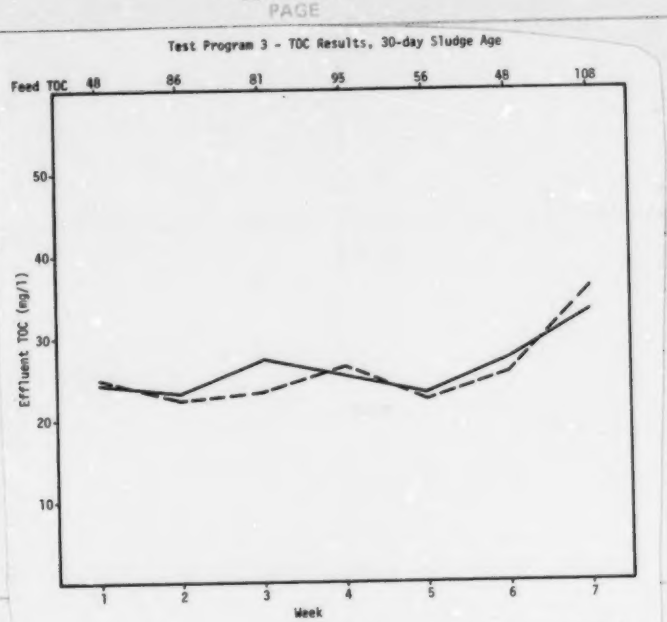

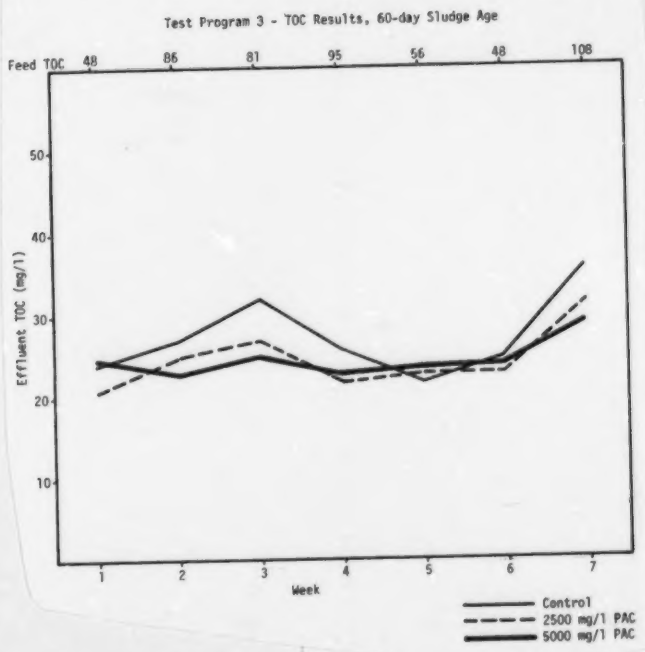

Figure 14. Test Program 3, weekly average total organic carbon.

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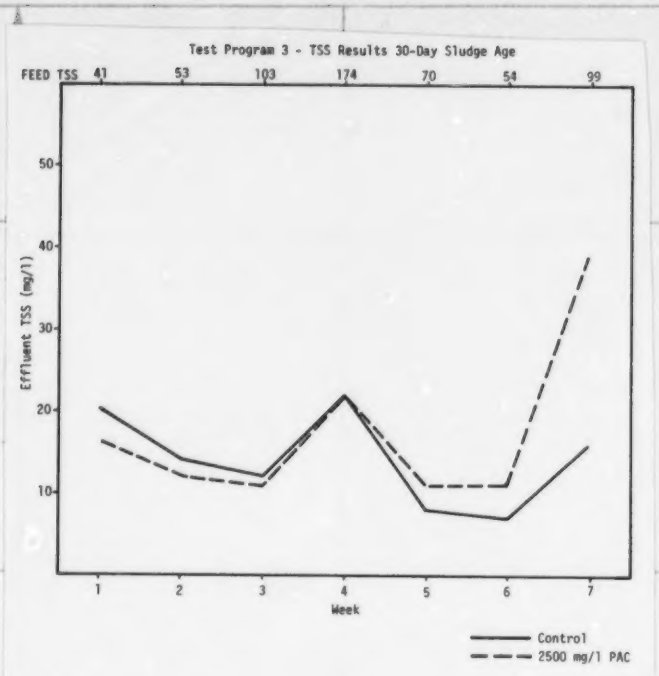

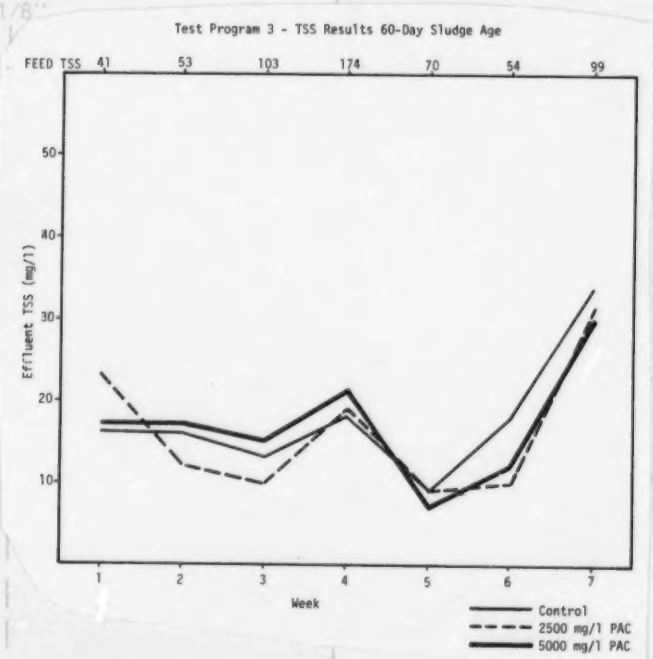
Test Program 3 - TSS Results 60-Day Sludge Age
FEED TSS 41 53 103 174 70 54 99
Effluent TSS (mg/l)
Week
Control
2500 mg/l PAC
5000 mg/l PAC

Figure 15. Test Program 3, weekly average suspended solids levels.

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Test Program 4

Test Program 4 was a continuation of Test Program 3 to determine if doubling the daily PAC makeup rate in Reactor E (PAC concentration = 5000 mg/1) would improve COD removal. Five laboratory-scale pilot units were operated in the following modes:

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A. Control, SA = 30 days
B. PAC = 2500 mg/1, SA = 60 days
C. PAC = 2500 mg/1, SA = 30 days
D. Control, SA = 60 days
E. PAC = 5000 mg/1, SA = 30 days

The average effluent concentrations are shown in Table 15 and the results of the statistical analysis are listed in Table 16. Figures 16-20 are graphs of the data.

The results showed no improvement by increasing the PAC concentration from 2500 mg/1 to 5000 mg/1 at a sludge age of 30 days. Effluent COD was 32% less from Reactors C and E than from the 30-day sludge age control. There was a 23% improvement in effluent COD in the PAC reactor at the 60-day sludge age in comparison with the control. The control reactors were statistically indistinguishable with regard to effluent COD.

The oil and grease results were similar to those in Test Program 3. The three PAC reactors were indistinguishable and performed significantly better than the controls. At the 30-day sludge age, there was a 39% improvement with a PAC concentration of 5000 mg/1 and a 33% improvement at a 2500 mg/1 PAC concentration. At the 60-day sludge age, there was a 21% improvement.

TOC removals were significantly higher in the control reactor at a 30-day sludge age. There was no significant difference in TSS and NH_3 concentrations from the five reactors.

The results of the statistical analysis in Test Program 4 were nearly identical to the results in Test Program 3. Despite the fact that the daily PAC makeup rate was twice as high in Reactor E than Reactor C, their performance was indistinguishable. This seems to indicate that there is an optimal PAC makeup rate. Adding more than the optimum does not result in improved performance.

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TABLE 15. SUMMARY OF RESULTS OF EFFLUENT QUALITY TESTS (AVERAGES, mg/1)--TEST PROGRAM 4

Parameter	A	B	C	D	E
Sludge Age (days)	30	60	30	60	30
Bio-Solids	2000	3200	2200	3000	2400
PAC	0	2500	2500	0	5000
PAC Addition Rate (mg/d)	0	417	833	0	1667
TOC	27.3	22.0	22.8	24.9	23.4
COD	47.1	36.2	31.9	47.0	32.0
NH_3-N	1.2	0.9	1.0	1.7	1.6
Oil and Grease	5.2	3.7	3.5	4.7	3.2
Suspended Solids	11.6	15.7	18.4	11.7	15.7

TABLE 16. SUMMARY OF STATISTICAL ANALYSIS--TEST PROGRAM 4

Parameter	Calculated F-value	Degrees of freedom	Signif-cance level	Groupings
TOC	4.09	4.28	0.99	(A),(B,C,D,E)
COD	36.1	4.100	>0.99	(A,D),(B),(C,E)
NH_3-N	1.56	4.76	0.81	--
Oil and Grease	7.38	4.28	>0.99	(A,D),(B,C,E)
Suspended Solids	2.18	4.96	0.92	--

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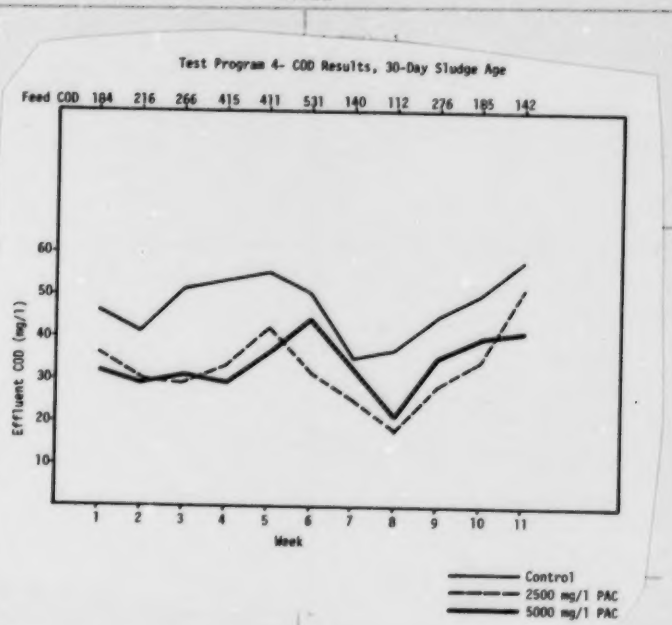
Test Program 4- COD Results, 30-Day Sludge Age
Feed COD 184 216 266 415 411 531 140 112 276 185 142
Effluent COD (mg/l)
Week
Control
2500 mg/l PAC
5000 mg/l PAC

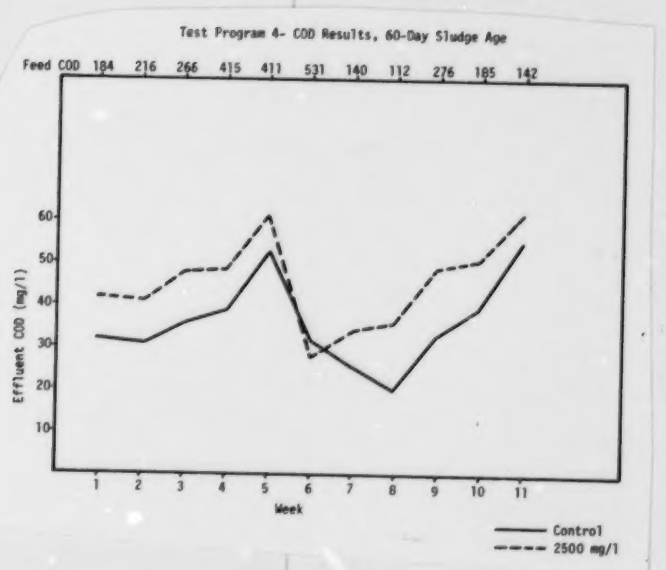
Test Program 4- COD Results, 60-Day Sludge Age
Feed COD 184 216 266 415 411 531 140 112 276 185 142
Effluent COD (mg/l)
Week
Control
2500 mg/l

Figure 16. Test Program 4, weekly average chemical oxygen demand levels.

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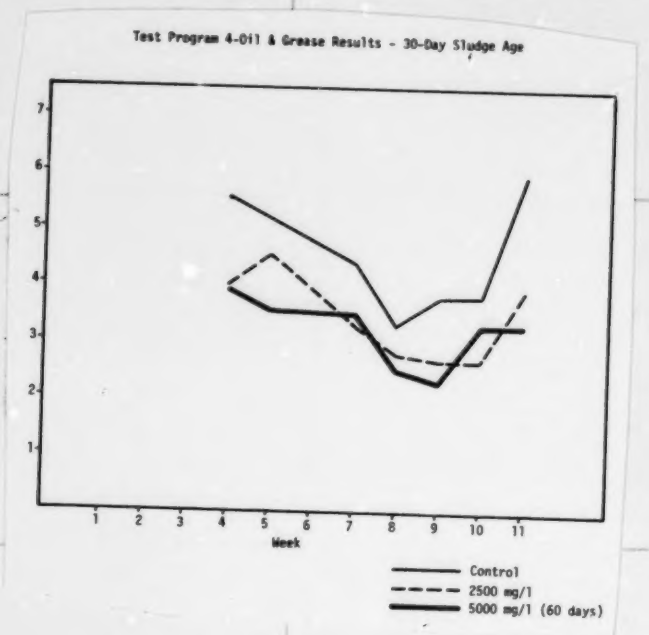

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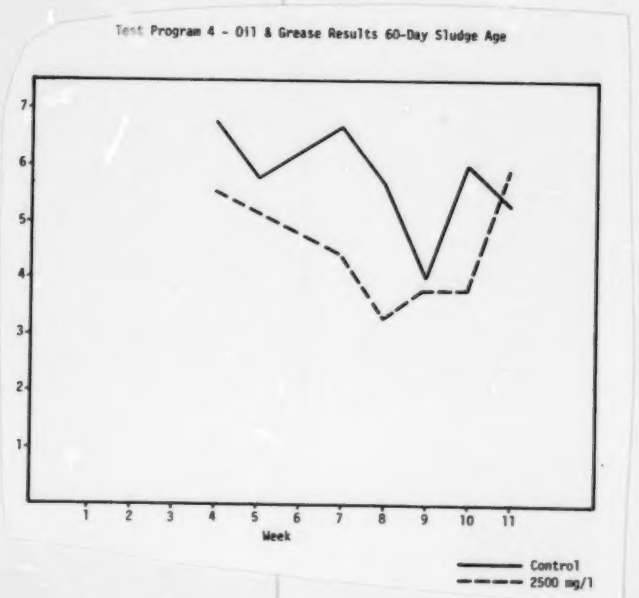

Figure 17. Test Program 4, weekly average oil and grease levels.

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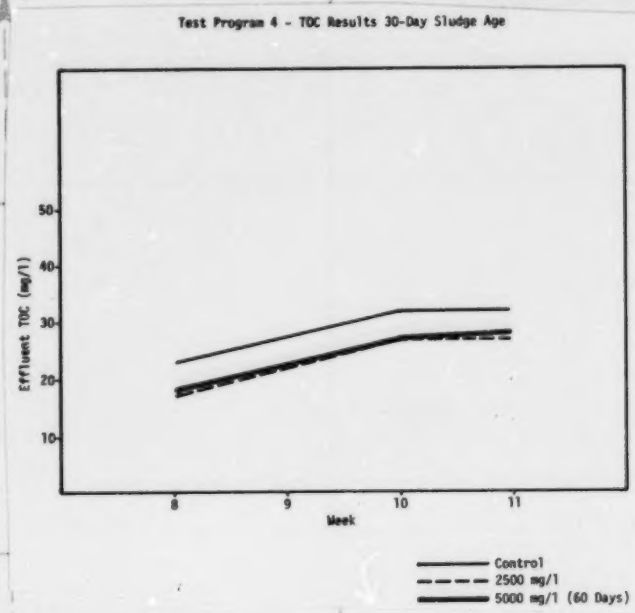

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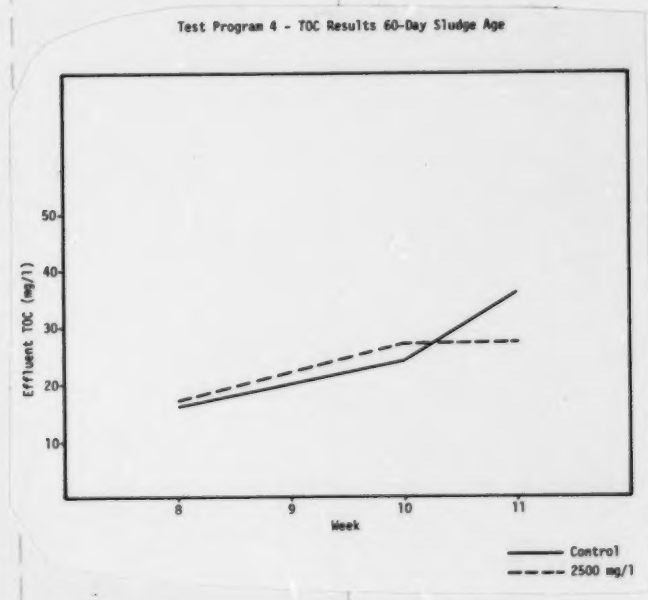

Figure 18. Test Program 4, weekly average total organic carbon levels.

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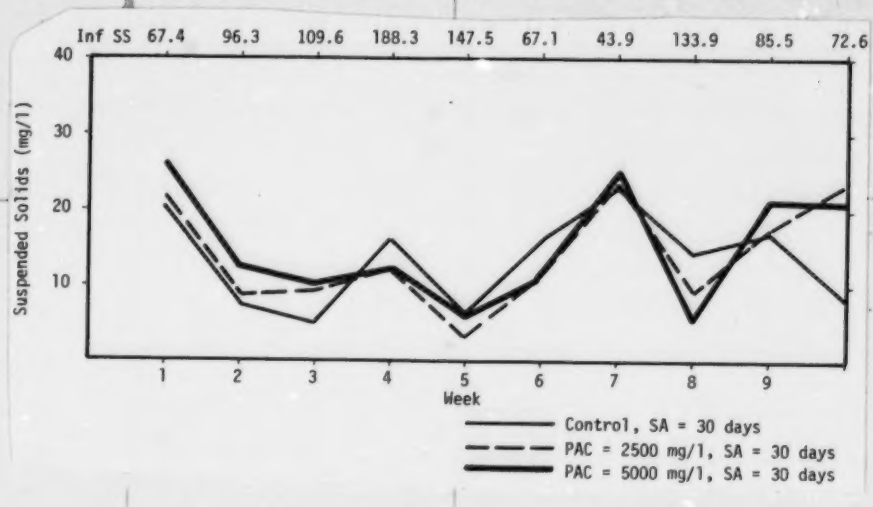

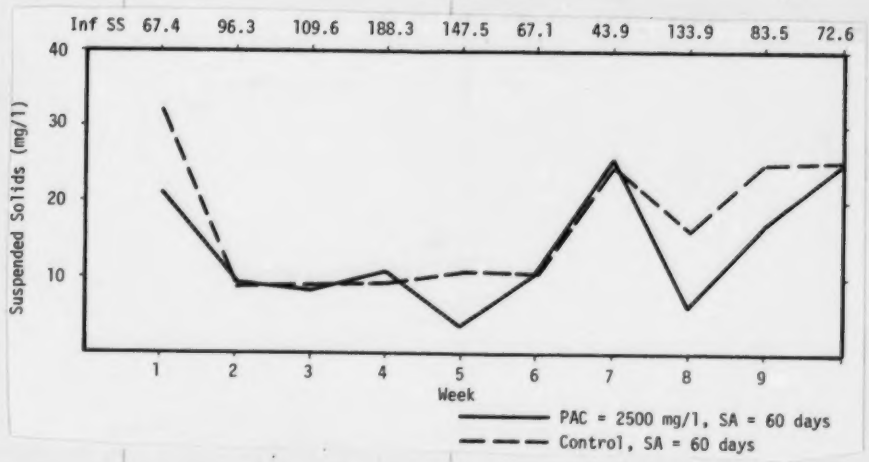

Figure 19. Test Program 4, weekly average suspended solids levels.

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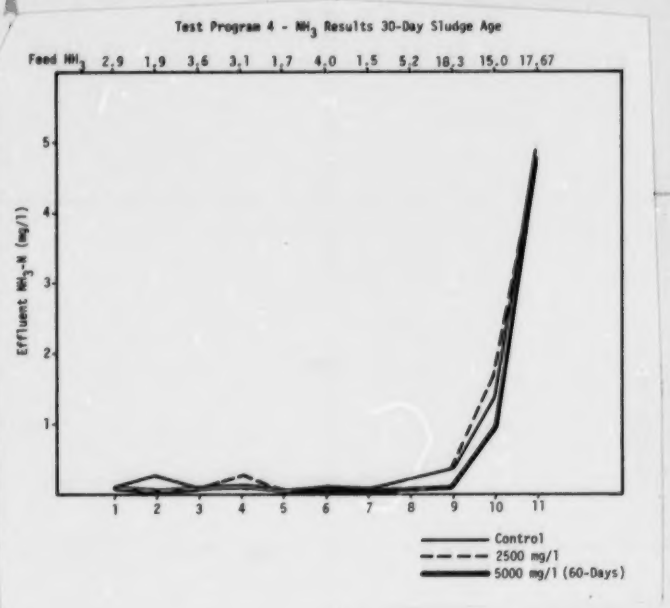
Test Program 4 - NH_3 Results 30-Day Sludge Age
Feed NH_3 2.9 1.9 3.6 3.1 1.7 4.0 1.5 5.2 18.3 15.0 17.67
Effluent NH_3-N (mg/l)
1 2 3 4 5 6 7 8 9 10 11
Control
2500 mg/l
5000 mg/l (60-Days)

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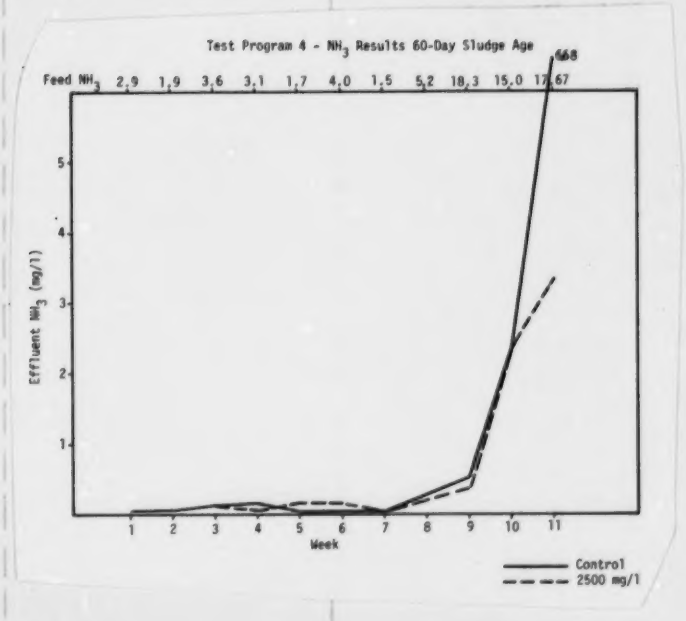
Test Program 4 - NH_3 Results 60-Day Sludge Age
Feed NH_3 2.9 1.9 3.6 3.1 1.7 4.0 1.5 5.2 18.3 15.0 17.67
668
Effluent NH_3 (mg/l)
1 2 3 4 5 6 7 8 9 10 11
Week
Control
2500 mg/l

Figure 20. Test Program 4, weekly average ammonia levels.

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SECTION 6

REFINERY STUDY

A full-scale refinery test to evaluate the effectiveness of PAC treatment was performed over a six-month period at the ARCO Point Breeze Refinery located in Philadelphia, Pennsylvania.

PROCEDURES

Treatment Scheme

The refinery wastewater treatment scheme is shown in Figure 21. The treatment scheme includes an API separator, pH control, dissolved air flotation, and activated sludge. Note that the system contains two parallel activated sludge reactors. The piping arrangement is such that the recycled sludge from one reactor can be kept completely isolated from the other. PAC was added to Reactor A which served as the experimental reactor. Reactor B served as the control. A slipstream of each effluent was pumped to pilot-scale dual media filters. Dual media filter effluent was used for water quality analysis and fish toxicity testing.

PAC Addition

PAC was added to Reactor A to a concentration of 1500 mg/1 over a 5-day period. A 40-day sludge age was maintained in both reactors. This corresponds to a 2.5% daily carbon makeup rate (5000 1b/week). The makeup carbon was added over the normal 5-day work week. A 3-week period was allowed for system acclimation before data gathering began. However, influent and effluent grab samples were obtained periodically and analyzed for TOC. The results are listed in Table 17. Initially, there was marked improvement in effluent TOC in Reactor A as compared to the control reactor. However, this difference was less marked by the third week and essentially disappeared by the fourth week. The addition of 28,000 1b of virgin carbon had a marked effect upon Reactor A performance. However, the daily makeup rate was not sufficient to maintain that difference.

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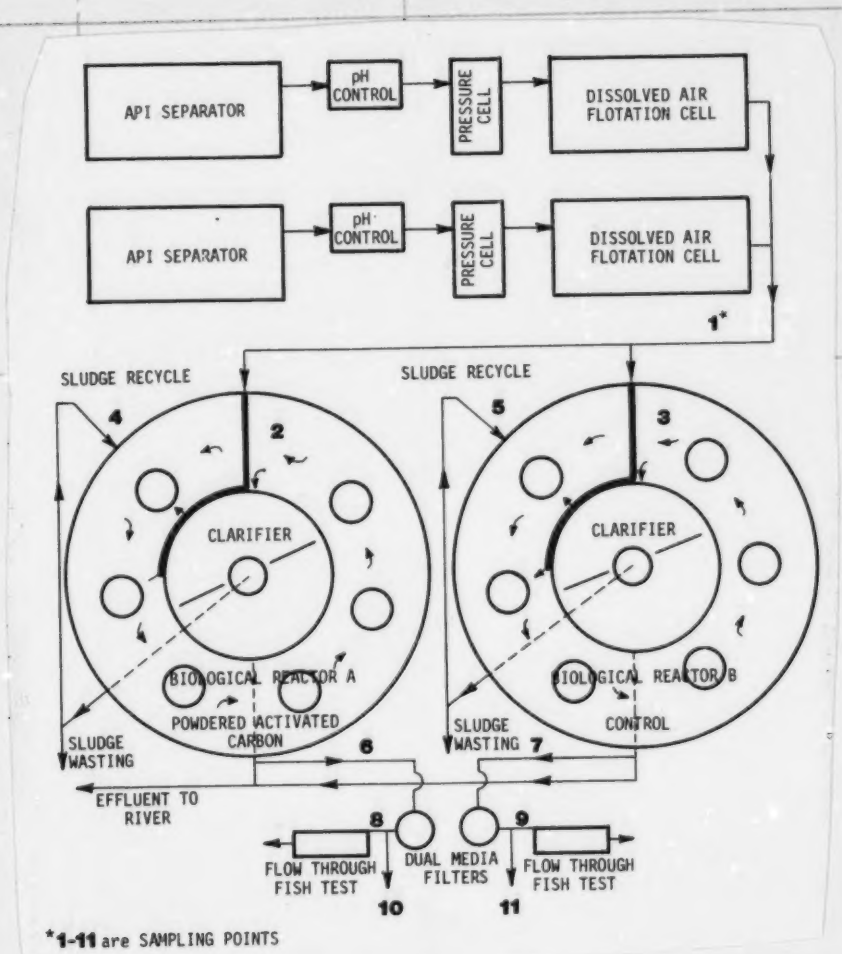

Figure 21. Diagram of wastewater treatment system at ARCO Refinery, Philadelphia.

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TABLE 17. EFFECT OF INITIAL PAC ADDITIONS ON TOC REMOVAL

Week	Average TOC (mg/1)* Eff. A	Eff. B	Influent
1	9	15	65
2	5	14	78
3	17	22	94
4	22	24	102

*Unfiltered Samples

Sludge Wasting

A 40-day sludge age was maintained in each reactor by wasting sludge from the sludge recycle lines. The waste sludges were kept separate. Waste sludge A was wasted to the thickener. Waste sludge B was wasted to the digester. This was done so that it would have been possible to seed either reactor with non-PAC sludge in the event of a major upset. The supernatant from the digestor and thickener flowed to Reactor A.

Statistical Analysis

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The data were analyzed using the paired-t test. The purpose of pairing the data was to eliminate the variation due to the influent conditions (Appendix A). Randomization is as important in the t-test as in the analysis of variance. Of course, it was not possible to randomly assign the PAC to one of the reactors each day. Reactor A was chosen as the PAC reactor at random at the onset of the test program.

Care was taken to insure that the operating conditions in the reactors were as similar as possible throughout the test. The flow was split as evenly as possible between the two reactors. Identical sludge recycle rates were maintained. The sludge wastage rate was adjusted so that the same sludge age was maintained in each system.

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EQUIPMENT

The four dual media filter columns were 5 feet in length, 6 inches in diameter, and were constructed of Pyrex. The endplates were stainless steel. Teflon gaskets were used. These filters contained the same depths of sand and anthrafilt as the filters described in the Bench-Scale Studies section. The hydraulic loading was about 2 gpm/ft^2

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ANALYTIC

Sampling

The effluent from the dual media filters was continuously sampled and collected in glass carboys. The carboys were kept in a refrigerator at a temperature of 2°C. The influent to the activated sludge reactors was the DAF effluent. A composite sampler was used to collect 24-hour composite samples of the activated sludge influent.

Grab samples of the recycle sludges and clarifier effluents were obtained once each shift. Grab samples of the MLSS were obtained once each day. These samples were analyzed for suspended solids and were used to make solids balances about the system. It was assumed that the fraction of PAC was the same in the clarifier A effluent stream as in the MLSS A and recycle A streams.

Methods

Test methods for water quality analysis were selected from EPA-approved procedures with one exception (16). Oil and grease analysis was performed with an OCMA-200 Oil Content Analyzer manufactured by Horiba Instruments. The instrument was chosen for its ease of operation and sensitivity in the low concentration range. The PAC concentration of MLSS A was determined by the procedure outlined in Appendix B. The analytic testing was performed inhouse. Table 18 lists the sample points, collection frequencies, and testing program. The sampling points refer to Figure 24.

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TABLE 18. SAMPLING AND ANALYTIC PROGRAM -- REFINERY TEST

Sampling Point	Sample	Analysis	Frequency
1	in Situ	ph, Conductivity	Continuous
	24-hour Composite	Oil and Grease, TOC, COD, NH_3, Suspended Solids	M, W, F
	24-hour Composite	Phenols	Occasionally
2,3	Grab	MLSS Concentration	Daily
	Grab	PAC Concentration	M, W, F
	In Situ	DO	Continuous
4, 5	Grab	Recycle Sludge	Daily, (once per shift)
6, 7	Grab	Suspended Solids	Daily, (once per shift)
8, 9	--	Fish Toxicity	--
10, 11	24-hour Composite	pH	M - F
	24-hour Composite	Oil and Grease, TOC, COD, NH_3, Suspended Solids	M, W, F
	24-hour Composite	Phenols	Occasionally

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RESULTS

Preliminary analysis of refinery effluents.

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Prior to the addition of PAC to Reactor A, a three-week sampling program of the refinery clarifiers was carried out. The purpose of the sampling program was to demonstrate that the two activated sludge units performed similarily under the same operating conditions. The reactors were operated with a sludge recycle rate of 550 gpm, which is the same as that used during the test. The sludge age was maintained at 35 days, slightly less than that maintained during the test.

Grab samples of the clarifier effluents (sampling points 6 and 7 in Figure 24) were obtained once each shift. The three grab samples obtained each day were combined to produce a daily composite sample. The composite samples were analyzed for TOC, oil and grease, TSS, and NH_3.The data are summarized in Table 19. The results of the paired t-test are shown in Table 20. The performance of the two activated sludge systems under these operating conditions were very similar. The effluent concentrations of TOC, oil and grease, TSS, and NH_3 were statistically indistinguishable.

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TABLE 19. SUMMARY OF RESULTS OF EFFLUENT QUALITY TESTS (AVERAGES, mg/1) -- PRELIMINARY REFINERY SAMPLING PROGRAM

Parameter	A	B
TOC	44.0	47.1
Oil and Grease	2.9	3.2
Suspended Solids	25.9	23.8
NH_3-N	3.7	3.5

TABLE 20. SUMMARY OF STATISTICAL ANALYSES -- PRELIMINARY REFINERY SAMPLING PROGRAM

Parameter	Calculated t	Degrees of freedom	Significance level
TOC	1.01	8	0.83
Oil and Grease	0.85	8	0.79
Suspended Solids	1.19	8	0.87
NH_3-N	0.59	8	0.71

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RESULTS

Test Program 5

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During the test period MLSS A averaged 5409 mg/1 and MLSS B averaged 3783 mg/1. The average PAC concentration was 1617 mg/1. The average influent flow was 3.1. The MGD average and the average sludge age was 41 days in each reactor. The recycle rate averaged 550 gpm. This information is listed in Table 21. There were considerable variations in the influent composition during the test. The influent data are summarized in Table 22.

Effluent data are summarized in Table 23. The data were statistically analyzed using the paired-t test. Plots of the influent and effluent data are shown in Figures 22-27. Note that the COD concentration was, on an average, 18% lower in effluent A than effluent B and that there was a 33% improvement in oil and grease concentrations. These results are very similar to those obtained in the laboratory-scale reactors.

There was very little NH_3 reduction in Reactor A. The effluent ammonia concentration was 74% lower in Effluent B. Throughout the test, the DO concentration was less than 1.0 mg/1 in Reactor A and greater than 1.5 mg/1 in Reactor B. It is reported in the literature that nitrification requires a minimum DO concentration of 1.5-2.0 mg/1. Since the DO oxygen concentrations in Reactor A were always considerably lower than that level, nitrification probably was not possible in that reactor. This may explain why NH_3 levels were higher in Effluent A.

TSS were significantly lower in Effluent B than Effluent A. This is not surprising since the solids loading on Clarifier A was 28% higher than on Clarifier B due to the PAC in Reactor A. The MLSS and recycle sludge volume indexes (SVI) were significantly lower in the PAC reactor than the control.

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TABLE 21. SUMMARY OF AVERAGE OPERATING CONDITIONS -- TEST PROGRAM 5

MLSS A	= 5409 mg/1
MLSS B	= 3783 mg/1
PAC	= 1617 mg/1
% PAC	= 28
Sludge Age	= 41 days
Flow	= 3.1 MGD
Recycle	= 550 gpm

TABLE 22. SUMMARY OF INFLUENT COMPOSITION -- TEST PROGRAM 5

Parameter	Range	Average	Median
TOC (mg/1)	58-610	193	138
COD (mg/1)	70-1560	437	312
NH_3 - N (mg/1)	3.6-22.0	10.9	9.0
Oil and Grease (mg/1)	25-460	124	60
Suspended Solids (mg/1)	18-692	118	41

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TABLE 23. SUMMARY OF RESULTS OF EFFLUENT QUALITY TESTS (AVERAGES, mg/1)--TEST PROGRAM 5

Parameter	A	B
Bio-Solids	3800	3800
PAC	1600	0
TOC	37.5	36.7
COD	41.1	50.1
NH_3-N	7.6	3.6
Oil and Grease	1.2	1.8
Suspended Solids*	26.7	21.3
Phenols	0.016	0.021
SVI - Recycle Sludge	55.5	75.4
SVI-MLSS	38.5	65.2

*Unfiltered grab samples

TABLE 24. SUMMARY OF STATISTICAL ANALYSIS--Test Program 5

Parameter	Calculated t	Degrees of freedom	Significance level
TOC	0.49	20	0.68
COD	2.59	16	0.99
NH_3-N	3.24	13	>0.99
Oil and Grease	4.16	19	>0.99
Suspended Solids	2.50	33	0.99
Phenols	1.19	3	0.84
SVI - Recycle Sludge	7.99	13	>0.99
SVI - MLSS	13.84	12	>0.99

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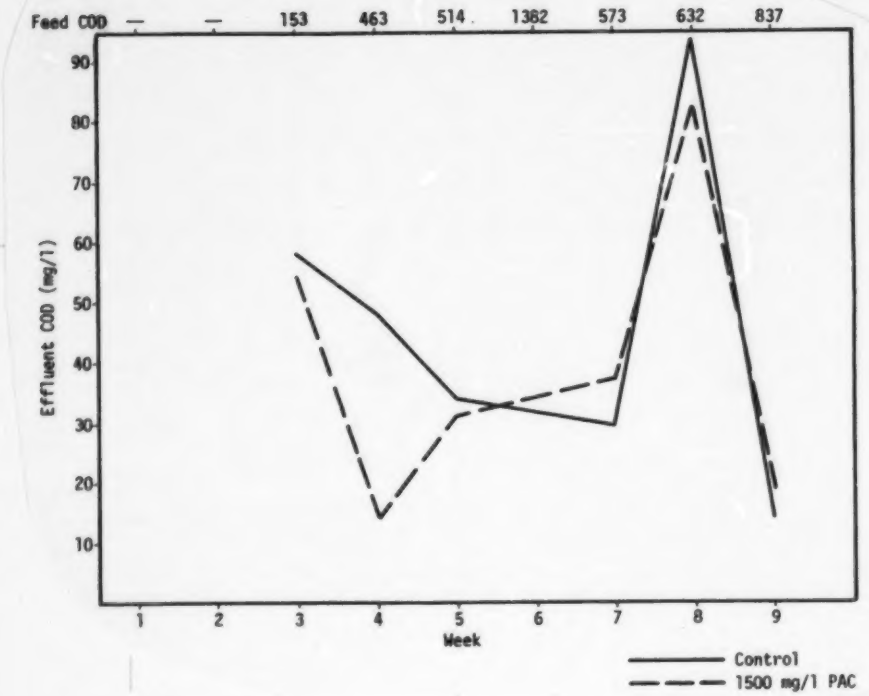

Figure 22. Test Program 5, weekly average chemical oxygen demand levels.

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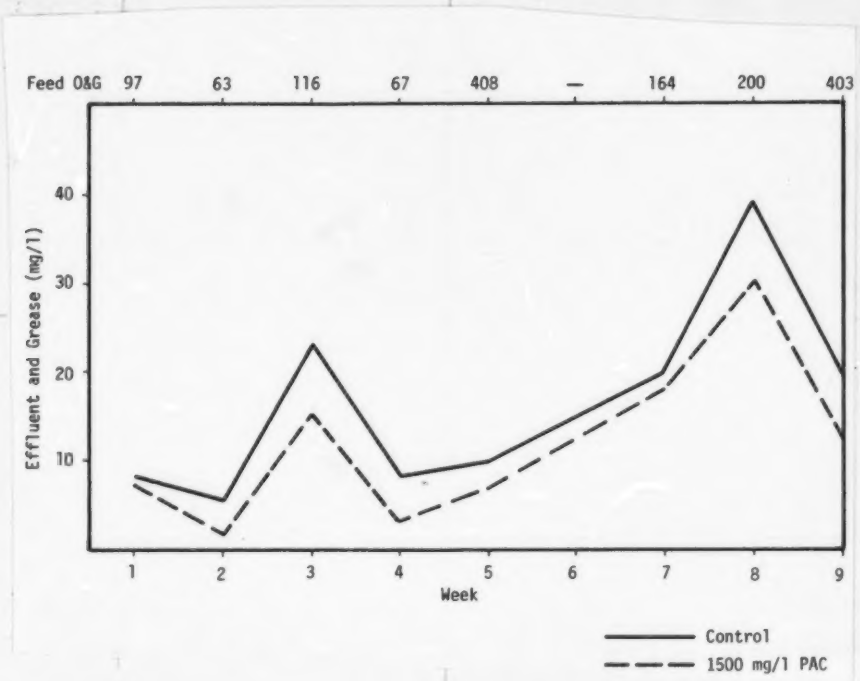

Figure 23. Test Program 5, weekly average oil and grease levels.

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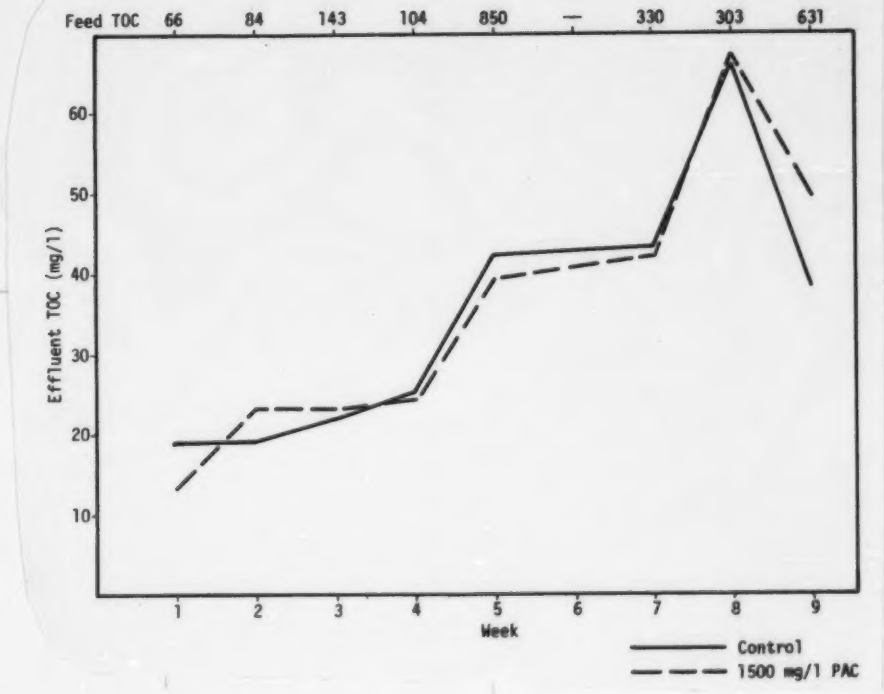

Figure 24. Test Program 5, weekly average total organic carbon levels.

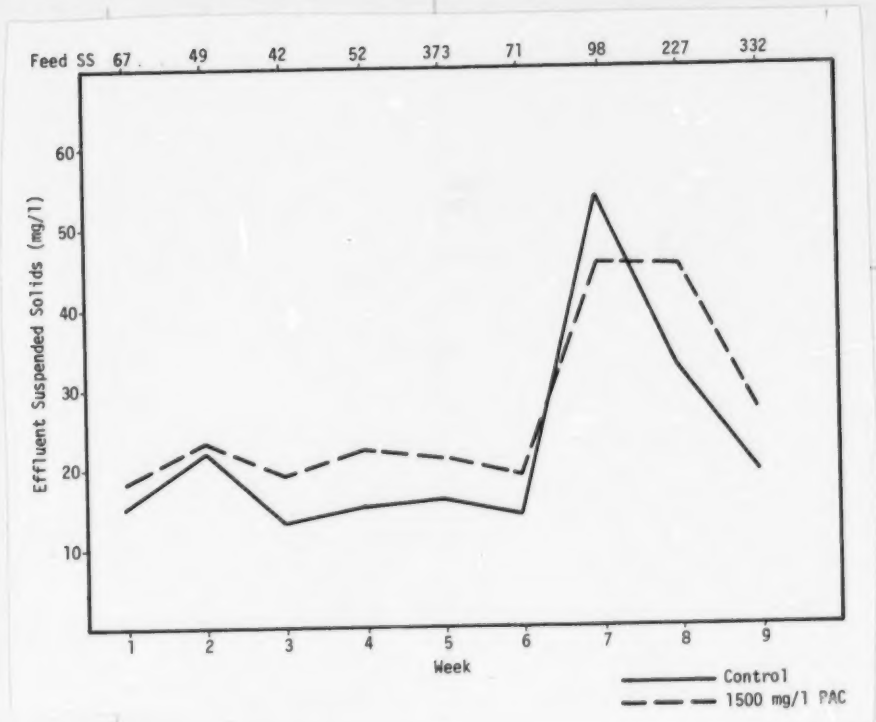

Figure 25. Test Program 5, weekly average suspended solids levels.

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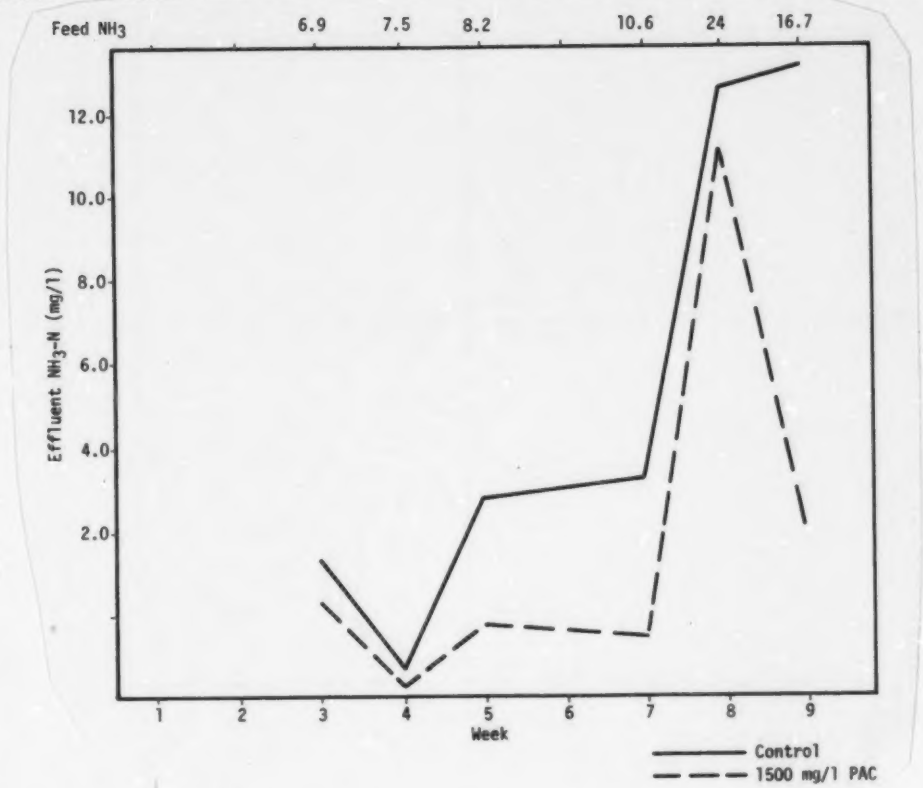

Figure 26. Test Program 5, weekly average ammonia levels.

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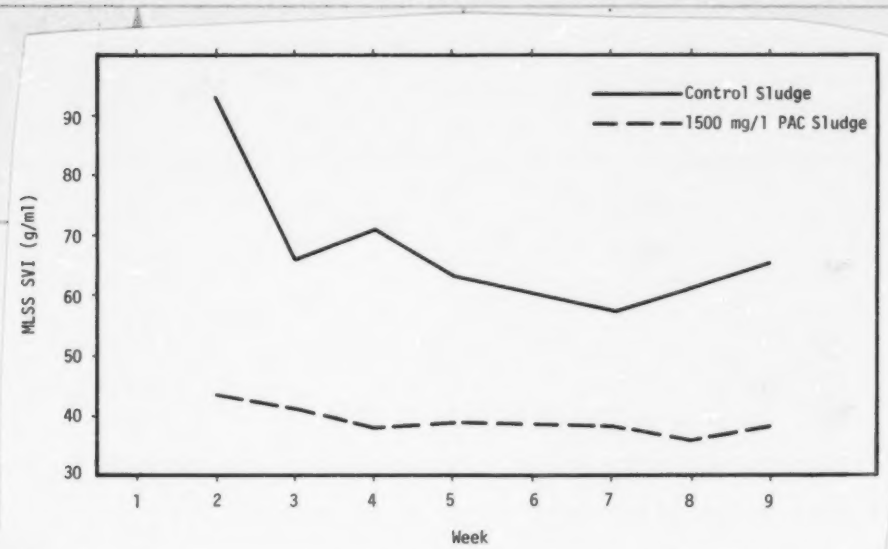

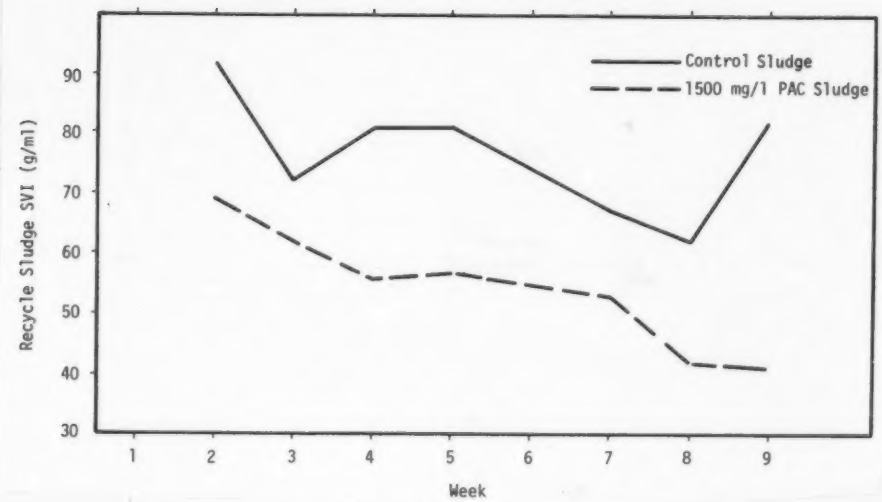

Figure 27. Test Program 5, weekly average sludge volume index values.

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Batch settling tests were carried out with sludge from the PAC and control reactors. Flux analysis was used to calculate the clarifier area requirements for both sludges. The flux curves are shown in Figure 28. The clarifier area required was determined for four different recycle sludge concentrations. The area requirements for the control sludge was calculated using the average control MLSS concentration observed during the test, 3783 mg/1. Likewise, the area requirements for the PAC sludge was calculated using the average PAC MLSS concentration, 5409 mg/1. The calculated areas are tabulated in Table 25. The required areas for the PAC sludge is considerably less than that required for the control sludge despite the fact that the PAC sludge was, on average, 1625 mg/1 greater than the control sludge. The actual area of each of the clarifiers at the Point Breeze Refinery is 6,221 ft^2.

TABLE 25. CALCULATED CLARIFIER AREAS

Recycle sludge concentration (mg/1)	Area required (ft^2)	
	PAC sludge	control sludge
16,000	2,540	3,053
18,000	3,407	4,247
20,000	4,506	4,884
22,000	5,372	5,921

The toxicity of the undiluted effluents from the PAC and control reactors was measured by conducting 96-hour, flow-through fish toxicity tests with Pimephales promelas. The fish toxicity tests were conducted in aerated, 10-gallon tanks. The flow through the tanks was adjusted to allow five turnovers daily. Fish to be tested were not fed for 24 hours prior to the onset of the test nor during the test period. At the onset of each test, the fish were placed in each of three tanks. The first tank received filtered, undiluted effluent from the PAC unit. The second tank received filtered, undiluted effluent from the control unit. The third tank received filtered, dechlorinated Philadelphia city tap water. The latter tank served as a control.

Seven sets of toxicity tests were carried out. None of the fish in the tap water control tank died during any of the tests. During five of the tests, none of the fish that were exposed to either the PAC effluent or control effluent died. During one test, one fish died in the control effluent tank while all survived in the PAC effluent. Finally, in one test, four fish died in the control effluent and three died in the PAC effluent. The data were analyzed statistically by the F-test. There was no statistically significant difference in the fish toxicity data.

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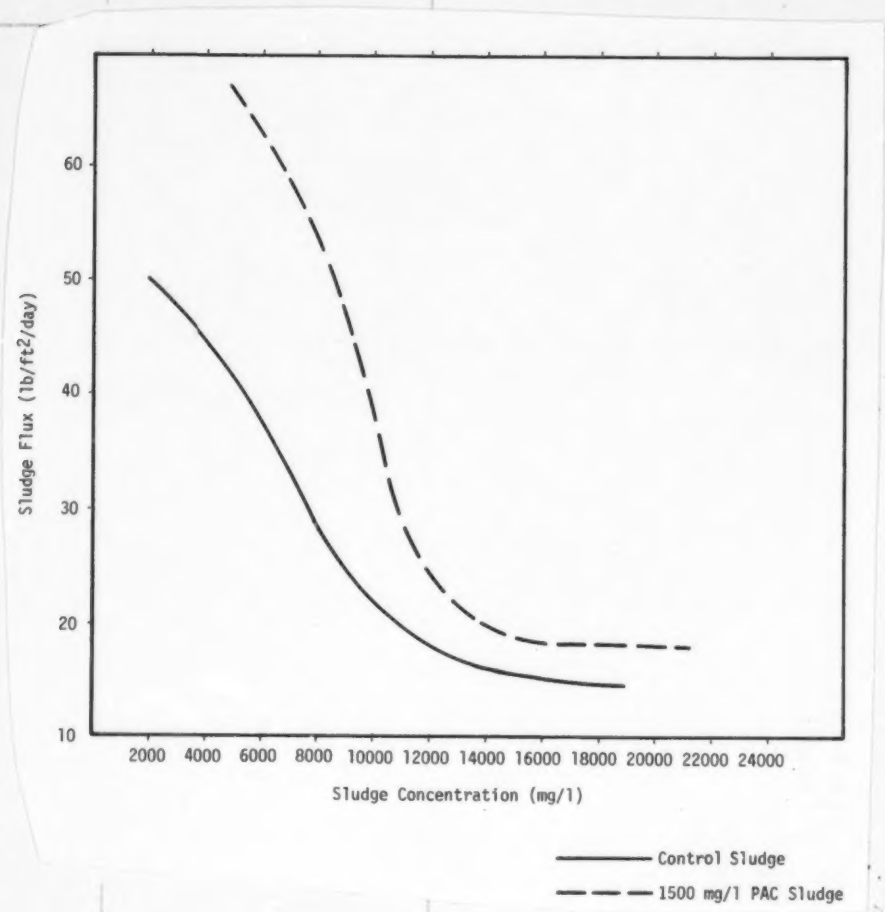

Figure 28. Sludge flux curves, Test Program 5.

The Robert S. Kerr Environmental Research Laboratory conducted a 3-day sampling program to obtain priority pollutant data. The samples were analyzed at that facility. Analytical results are listed in Table 26 (17). The concentrations of the priority pollutants were not significantly lower in effluent A than in effluent B.

The following conclusions can be drawn from Test Program 5:

1. The addition of 1600 mg/1 PAC with a 2.5% makeup rate resulted in an 18% reduction in COD and 33% reduction in oil and grease compared to the control. This is equivalent to an overall improvement in COD reduction of 2%.

2. There was a 75% reduction in effluent NH_3 from the control reactor as compared to Reactor A. The DO concentrations less than 1.0 mg/1 in Reactor A probably account for this.

3. Effluent TSS were 28% higher from Reactor A than Reactor B. The sludges from the PAC reactor packed more readily as indicated from the significant improvement in SVI.

4. PAC had no significant effect on effluent priority pollutant concentrations.

Test Program 6

An attempt was made to continue the refinery test at a PAC concentration of 2500 mg/1. An additional 19,500 lbs of PAC was added to Reactor A to increase the PAC concentration to 2500 mg/1. Within a week of the PAC addition, there was a 65 % reduction in MLSS A. The sludge had settled to the bottom of the A aeration tank. Attempts were made to use diffusers to raise the sludge. A portion of the sludge did rise from the bottom. However, efforts to raise the sludge were hampered by the breakdown of several aerators in the A aeration tank. After six weeks, the project was abandoned.

Comparison of Bench-Scale and Refinery Studies

The average effluent quality results for the first two bench-scale tests and the refinery test are tabulated in Table 27. An examination of the table shows that, with the exception of NH_3, the effects of PAC addition were comparable in all three test programs. There was a 15.1% improvement in effluent COD in Test Program 1, 13.2% and 23% improvements in Test program 2, and 17.6% improvement in the refinery study. There was a 37.5% improvement in effluent oil and grease in Test Program 1, 29.4% and 30.4% improvement in Test Program 2, and 33.3% in Test Program 3. The bench-scale units seem to be good indicators of refinery performance.

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TABLE 26. RESULTS OF PRIORITY POLLUTANT ANALYSES (17)

Priority pollutant	Influent (µg/1)	PAC return sludge (µg/1)	Return sludge (µg/1)	PAC effluent (µg/1)	Final effluent (µg/1)
CLASSICAL					
TOTAL CYANIDES (mg/1)*	<.05	<.05	<.05	<.05	<.05
TOTAL PHENOL	417	386	67	42	29
TOTAL METALS					
Arsenic	< 10	260	150	< 10	< 10
Selenium	< 10	400	280	< 10	< 10
Cadmium	< 1	31	24	< 1	< 1
Beryllium	< 3	20	9	< 3	< 3
Copper	45	5,800	4,900	18	16
Antimony	< 10	< 10	< 10	< 10	< 10
Chromium	280	64,000	60,000	100	72
Nickel	17	1,200	1,100	14	17
Zinc	390	37,000	28,000	140	130
Silver	< 10	22	22	< 10	< 10
Thallium	< 10	< 10	< 10	< 10	< 10
Lead	40	12,000	11,000	18	14
Mercury	<0.6	< 10	< 10	<1.0	<0.8
ORGANICS (GAS CHROMATOGRAPHY)					
PURGEABLES					
Methylene chloride	< 10	N.A.	N.A.	< 10	< 10
Chloroform	< 10	"	"	< 10	< 10
Benzene	320	"	"	< 40	< 40
1,1,2,2,-Tetrachloroethylene	< 10	"	"	< 10	< 10
Toluene	695	"	"	< 10	< 10
Ethylbenzene	56	"	"	< 10	< 10
POLYNUCLEAR AROMATICS					
Pyrene	< 10	< 12	< 13	< 10	< 10
Benzo-a-pyrene	< 44	<106	<110	< 13	< 11
Chrysene	< 10	< 14	< 14	< 10	< 10
Fluoranthrene	< 10	< 12	< 13	< 10	< 10
Phenanthrene/Anthracene	<10/<10	<14/<16	<14/<17	<10/<10	<10/<10
Naphthalene	282	< 14	< 14	< 10	< 10
Acenaphthene	24	< 10	< 10	< 10	< 10
Fluorene	< 16	< 39	< 41	< 10	< 10

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TABLE 26. (Continued)

Priority pollutant	Influent (µg/1)	PAC return sludge (µg/1)	Return sludge (µg/1)	PAC effluent (µg/1)	Final effluent (µg/1)
PHENOLS					
2,4-dimethylphenol	N.S.	N.S.	N.S.	N.S.	N.S.
PHTHALATE ESTERS					
Dimethyl phthalate	<10	<10	<10	<10	<10
Diethyl phthalate	<10	<10	<10	<10	<10
Di-n-butyl phthalate	<10	<10	<10	<10	<10
Bis(2-ethyhexyl)phthalate	<16	<16	<16	<16	<16

*Note: Total Cyanides expressed in mg/1.

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TABLE 27. COMPARISON OF BENCH-SCALE AND REFINERY TEST RESULTS (AVERAGES)

Parameter	Bench-scale test program 1		Bench-scale test program 2				Refinery	
Bio-Solids (mg/l)	2000	2000	2000	2000	4000	4000	3800	3800
Powdered Activated Carbon (mg/l)	0	1500	0	2000	0	2000	0	1600
Chemical Oxygen Demand (mg/l)	33.1	28.1	50.0	43.4	53.8	43.7	50.1	41.1
Total Organic Carbon (mg/l)	16.6	15.3	10.6	14.8	12.1	15.0	36.7	37.5
Oil & Grease (mg/l)	2.4	1.5	1.7	1.2	2.3	1.6	1.8	1.2
Ammonia Nitrogen (mg/l)	0.7	0.6	0.4	0.3	1.6	0.8	3.6	7.6

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SECTION 6

DISCUSSION

Throughout this study the control units produced a good quality effluent so that the addition of PAC had only a moderate effect upon system performance. Units were operated at PAC concentrations of 500 - 5,000 mg/1 and at sludge ages of 30 - 60 days. COD and oil and grease removals were enhanced by PAC addition in all test programs. PAC addition had no effect on the removal of TOC or phenol. PAC addition had little effect on NH_3 removal except during the refinery test. During the refinery test, the NH_3 concentration in the control effluent averaged 53% less than in the effluent from the PAC unit.

Greater sludge settleability, greater sludge compactability, and more consistent effluent quality are other advantages that were observed with PAC addition. During the refinery test, several disadvantages of the process became apparent. The presence of the PAC increased the solids loading on the secondary clarifier by about 40,000 lb/day and resulted in a 20% increase of TSS in the effluent from the PAC reactor. It is known that PAC is abrasive. After the termination of the refinery test, increased wear of the pumps used to recycle the PAC sludge was observed. In addition, PAC sludge appears to have greater mixing requirements than conventional activated sludge. During the refinery test, there were no apparent problems in keeping the PAC sludge in suspension when the PAC concentration was 1,600 mg/1. However, when additional carbon was added in an attempt to increase the PAC concentration to 2,500 mg/1, a considerable portion of the PAC sludge settled to the bottom of the aeration basin. Mixing was provided by six surface aerators with a total of 150 hp. Although it is not possible to quantify the magnitude of the increase, an increase in the size or number of aerators, with an associated increase in the process power requirement, would have been required to maintain the higher concentration of PAC in suspension.

The experimental results suggest that the degree of enhancement is related to the daily carbon makeup rate and not to the concentration of PAC maintained in the aeration basin. In Test Program 1, units were operated with PAC concentrations of 500 mg/1, 1,000 mg/1, and 1,500 mg/1. However, the daily carbon makeup rates were similar for each reactor. The performance of the three reactors was statistically indistinguishable. During Test Program 3, two units were operated with PAC concentrations of 2,500 mg/1. The carbon makeup rate was 833 mg/day to one of the units and 417 mg/day to the other. A third reactor was operated at a PAC concentration of 5,000 mg/day with a PAC makeup rate of 833 mg/day. The performance of the two units with the makeup rate of 833 mg/day was indistinguishable de-

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spite the fact that twice as much PAC was maintained in the aeration basin of the 5,000-mg/1 PAC unit. The two reactors with the makeup rate of 833 mg/day out-performed the unit with the carbon makeup rate of 417 mg/day. These results are similar to those reported by Thibault et al. (10,11), the API (14, 15), Stenstrum and Grieves (12), and Grieves et al. (12). In all of those studies, the best effluent quality was observed in those units which received the highest daily carbon makeup dosage. In addition, there appears to be a daily makeup rate above which there is no further enhancement. During Test Program 4, there was no statistically significant difference in the performance of units receiving a carbon makeup dosage of 833 mg/day or 1,667 mg/day.

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Because the performance is related to the PAC makeup rate and is independent of the PAC concentration, the main mechanism of enhancement of COD removal appears to be absorption. Bioregeneration of the surface of the carbon as has been reported by Flynn et. al. (3) and Robertaccio (5), did not seem to occur with the refinery wastewater. The results of the oxygen uptake tests also support this conclusion. There was no statistically significant difference in the oxygen uptake rates between the control and PAC reactors during the benchscale tests.

The degree of enhancement observed in this study is less than that reported by the API (14, 15), Stenstrum and Grieves (12), and Grieves et al. (13). There are several factors which may have contributed to this. First of all, the control reactors in this study generally performed better than those in the other studies. This is shown in Table 28. Note also that the values reported by the others are generally soluble TOC and COD (samples were filtered through Millipore filters prior to analysis) so that the actual differences in control reactor performance are even greater than shown. This is not a criticism of those studies. The differences in control performance are probably related to the characteristics of the wastewater. Clearly, the poorer the performance of the control units, the greater the potential for PAC enhancement. This implies that the effect of PAC addition will vary for each application depending upon the performance of the existing activated sludge unit.

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TABLE 28. A COMPARISON OF CONTROL REACTORS PERFORMANCE (AVERAGES, mg/1)

	TOC (mg/1)	COD (mg/1)
API - Phase I [α]		
Part 1	56, 58, 64	105, 108, 128
Part 2	44, 46, 68	108, 111, 163
API -Phase II [α]	43	--
Stenstrum and Grieves [α]	22, 26, 26.5	58, 66, 73
Grieves et al. [α]	21, 22	68, 74
Present Work		
Test Program 1	17	33
Test Program 2	11, 12	50, 54
Test Program 3	25, 26	49, 52
Test Program 4	25, 27	47, 47
Test Program 5	37	50

[α] Reported soluble TOC and COD

Secondly, relying on soluble TOC or soluble COD to evaluate system performance exaggerates the degree of enhancement that is observed. By filtering the samples through Millipore filters prior to analysis, only PAC-free samples are analyzed. PAC has a TOC and a COD and the organics adsorbed on the surface of the carbon also have a TOC and a COD. If the effluent contains PAC, a portion of the effluent TOC and COD is associated with the presence of the PAC. Current EPA regulations do not allow the filtration of samples prior to analyses performed to satisfy the requirements of NPDES permits. Nor is it possible to achieve the same degree of solids removal by filtration of the effluent from a full-scale plant as is possible in the laboratory. Thus, the enhancement results reported in those studies should be regarded as an upper limit for the process which can never be practically achieved. Thibault et al. (10) have reported filtered and unfiltered COD's and TOC's. The average COD in the effluent from the PAC unit was 20% less than in the control effluent prior to filtration. After filtration, the average COD in the PAC effluent was 44% less than in the control effluent. Similar results were reported for the TOC's. Occasionally during this study, filtered and unfiltered samples were analyzed. The difference in effluent COD from the PAC and control units always increased after filtration. Filtration had less of an effect upon the TOC's in this study. In a full-scale plant, the best that can be done is to remove as much of the effluent PAC as possible by sand or multimedia filtration. That is why dual media filters were used here. However, since the filtration rates used in this study were unrealistically low (0.5 gpm/ft² and 2 gpm/ft² vs. the conventional 5 - 15

gpm/ft^2), the degree of enhancement observed here may also be greater than can be practically achieved.

Finally, in the other recent studies, the greatest enhancement was observed in those units in which the high-surface-area experimental carbon was used. This carbon is not now commercially available. It is not known if it will ever be commercially manufactured nor what it would cost if it were available. Thus, it did not seem prudent to evaluate the PAC technology with the experimental carbon. It is possible that greater enhancement would have been observed in this study had the experimental carbon been used.

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SECTION 8

ECONOMICS

An economic analysis was carried out to assess the cost of implementing the PAC addition program that was tested at the Point Breeze Refinery. If such a program were implemented, it would be necessary to install a system to receive bulk shipments of PAC, to store bulk PAC, to meter the daily PAC dosage, and to slurry the PAC prior to its introduction into the aeration basins. Since the degree of COD enhancement is partially a function of the efficiency of PAC removal from the secondary clarifier effluent, it is necessary to filter the secondary clarifier effluent. If the wastewater treatment scheme does not include filtration, as is the case at the Point Breeze Refinery, such equipment would have to be installed.

Capital requirements for the carbon handling and filtration equipment were obtained by requesting price quotations frm equipment vendors. Table 27 lists the results of the economic calculations. The annual cost includes capital amortization at a rate of return of 12% over a 20-year period. Equipment life expectancy is 20 years and a zero salvage value was assumed. If only the costs of the carbon handling system and the daily PAC requirement are considered, the annual cost is $225,500. This corresponds to an incremental cost of $2.54/lb. of COD removed and $38.11/lb. of oil and grease removed. If the cost of filtration is included, the annual cost is $603,500. This corresponds to an incremental cost of $7.00/lb. of COD removed and $105/lb. of oil and grease removed.

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TABLE 29. ECONOMIC ANALYSIS - ANNUAL COSTS

Cost	PAC System	Filtration	Total
PAC Makeup	$182,500	-	$182,500
Operating & Maintenance	10,000	$ 70,000	80,000
Capital Amortization	33,000	308,000	341,000
	$225,500	$378,000	$603,500

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APPENDIX A

DESCRIPTION OF STATISTICAL TECHNIQUES

ANALYSIS OF VARIANCE

The analysis of variance is a statistical technique for comparing the results from more than two experimental treatments. As the name implies, the technique is used to estimate how much of the total variation in a set of data can be attributed to one or more assignable causes. The remainder, not attributable to any assignable cause, is classified as the residual or error variation. The F-test is then used to determine whether the assignable causes resulted in real variation or whether the variation is due to chance.

Two-way analysis of variance makes use of two assignable causes, the tratment variable and the blocking variable. An assumption of the two-way analysis of variance is that the data can be described by a simple additive model:

$$Y_{ti} = n + \beta_1 + \tau_t + \varepsilon_{ti}$$

Where:

Y_{ti} = An observation using the t^{th} treatment in the i^{ti} block

n = Mean of the data set

β_1 = Effect of i^{th} block; independent of treatment

τ_t = Effect of the t^{th} treatment; independent of block

ε_{ti} = Error associated with observation

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If the additive model is true, each observation can be decomposed into four terms:

$$\underset{\text{Observation}}{Y_{ti}} = \underset{\text{Grand Average}}{\bar{Y}} + \underset{\text{Block Deviation}}{(\bar{Y}_i - \bar{Y})} + \underset{\text{Treatment Deviation}}{(\bar{Y}_t - \bar{Y})} + \underset{\text{Residual}}{(\bar{Y}_{ti} - \bar{Y}_i - \bar{Y}_t + \bar{Y})}$$

Where:

$\bar{Y}$ = Grand average of data set

$\bar{Y}_i$ = Average of i^{th} block

$\bar{Y}_t$ = Average of t^{th} treatment

All of the data can be decomposed in this manner. If each term of the decomposition is squared for all of the data and the squares for each term are summed, the sums of squares for the observations, grand average, block effects, treatment effects and residuals are obtained. Table 30 shows the general formulas for the decomposition of the sume of the squares as well as the degrees of freedom for the case of k treatments and n blocks.

TABLE A-1. FORMULAS FOR THE DECOMPOSITION OF THE SUMS OF SQUARES

Source of variation	Sum of squares	Degrees of freedom
Between Treatments	$S_T = n \sum_{t}^{k} (\bar{Y}_t - \bar{Y})^2$	k-1
Between Blocks	$S_B = k \sum_{i}^{n} (\bar{Y}_i - \bar{Y})^2$	n-1
Residual	$S_R = \sum_{t}^{k} \sum_{i}^{n} (\bar{Y}_{ti} - \bar{Y}_t + \bar{Y})^2$	(k-1) (n-1)

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The mean squares are obtained by dividing the sum of the squares by degrees of freedom for each source of variation. If the residuals are randomly distributed with mean zero and variance σ^2, the expected value of the residual mean square, S_T^2 is also σ^2, regardless of the treatment and block effects. If all of the treatment means are equal, the expected value of the treatment mean square, S_T^2 is also σ^2. However, if the treatment means differ, this mean square will be inflated by $n \varepsilon \tau_t^2 / k-1$. Likewise, if all the block means are equal, the expected value of the block mean square is σ^2. If the block means differ, the block square will be inflated by $k \varepsilon \tau_i^2 / n-1$. Table A-2 shows the method of calculation of the mean squares as well as their expected values.

TABLE A-2. MEAN SQUARES - EXPECTED VALUES AND METHODS OF CALCULATION

Source of variation	Degrees of freedom	Mean square	Expected value of mean squares
Between Treatments	k-1	$S_T^2 = S_T/k-1$	$\sigma^2+n \varepsilon \tau_t^2/(k-1)$
Between Blocks	n-1	$S_B^2 = S_B/n-1$	$\sigma^2+ k \varepsilon \beta_i^2/(n-1)$
Residuals	(k-1) (n-1)	$S_R^2 = S_R/(k-1)(n-1)$	σ

If the term $n \varepsilon \tau_t^2 / (k-1)$ or $k \varepsilon \beta_i^2 / (n-1)$ is much greater than σ^2, the ratio S_T^2/S_R^2 or S_B^2/S_R^2 will be much greater than 1. If S_T^2/S_R^2 is much greater than 1, the treatment effect is much greater than the error and one might have confidence that the differences in the treatment means is not due to chance. Likewise, if the ratio S_R^2/S_R^2 is much greater than 1, one would have confidence that differences in the blocks means were not random. The use of the F-test makes it possible to quantify the significance level of differences in the block or treatment means. The ratios of S_T^2/S_R^2 and S_B^2/S_R^2 are referred to the F-distribution with the appropriate degrees of freedom. It is thus possible to test the hypothesis that all τ_t or all B_i are equal to zero.

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DUNCAN'S NEW MULTIPLE RANGE TEST

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The analysis of variance and the F-test are a means of determining whether or not there are significant differences between treatment means. However, the procedures do not identify which means are significantly different from the others. Duncan has developed a procedure known as the new multiple range test to identify those means which are significantly different.

The first step of the procedure is to calculate the standard error of the means from

$$S_M = S_R^2/n$$

where:

S_M = Standard error of the means

S_R^2 = Residual means square

n = Number of terms making up each mean

The degrees of freedom of the standard error is equal to the number of degrees of freedom of the residual term in the analysis of variance.

The second step of the procedure is to obtain the p-1 significant studentized ranges where p is the number of experimental treatments. The significant studentized ranges are obtained from tables using the appropriate degrees of freedom. The third step of the procedure is to calculate p shortest significant ranges (SSR) from the products of the standard error and the significant studentized ranges.

The final step of the procedure is to determine the significance of the differences between the treatment means. This is done by subtracting the smallest mean from the largest and comparing the difference to the pth SSR. If this difference is greater than the SSR, the means are significantly different. The second smallest mean is then subtracted from the largest and the difference is compared to the p-1 SSR. If this difference is greater than the SSR, the means are significantly different. This procedure is continued until all differences between all of the means are calculated and compared to the appropriate SSR.

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PAIRED t-TEST

The t-test is a statistical technique to test the significance of differences in results from two experimental treatments. Pairing the results from each day made it possible to eliminate the effects of the daily fluctuations in the influent concentration.

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The differences, d, between Treatment A and Treatment B are calculated for each day. The value of t is calculated from:

$$t = \frac{\bar{d} - \delta}{S_d/n}$$

where:

$\bar{d}$ = Average difference

δ = Expected difference

S_d = Standard deviation of the differences

n = Number of data pairs

The standard deviation is:

$$S_d = \frac{\varepsilon\, d^2 - (\varepsilon\, d)^2/n}{n-1}$$

For the null hypothesis, $\delta = 0$. The significance level for the calculated t is determined for n-1 degrees of freedom.

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APPENDIX B

METHOD OF DETERMINING PAC CONCENTRATION

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PROCEDURE

The PAC concentration of PAC/bio-solids mixtures was determined by digestion with HNO_3. The procedure is described below:

1. Prepare a solution of PAC that approximates the PAC concentration in the PAC MLSS.

2. Determine suspended solids concentration of PAC MLSS, control MLSS, and PAC solution.

3. Add 25 ml of concentrated HNO_3 to three 250-ml Erhlenmeyer flasks. Add 50 ml of PAC MLSS to the first flask, 50 ml of control MLSS to the second flask, and 50 ml of PAC solution to the third.

4. Heat contents of flasks to boiling and boil for 15 minutes.

5. Let flasks cool. Determine suspended solids of digested solutions.

6. Calculation of PAC concentration in PAC MLSS:

$$P = \frac{AM - M'}{A - B}$$

where:

P = PAC concentration in PAC MLSS (mg/1)

M = Concentration of PAC MLSS (mg/1)

M' = Concentration of PAC MLSS after acid digestion (mg/1)

$$A = \frac{\text{Control MLSS concentration (after acid digestion)}}{\text{Control MLSS concentration (before acid digestion)}}$$

$$B = \frac{\text{Control PAC concentration (after acid digestion)}}{\text{Control PAC concentration (before acid digestion)}}$$

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DERIVATION OF EQ. 1

The concentration of the solids in the PAC/bio-solids mixture is equal to the sum of the PAC concentration and the bio-solids concentration:

$$M = P + S \qquad (2)$$

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where:

M = Concentration of PAC/bio-solids mixture

P = Concentration of PAC

S = Concentration of bio-solids

A similar expression can be written for the solids concentration of the mixture after HNO_3 digestion:

$$M' = P' + S' \qquad (3)$$

where:

M' = Concentration of PAC/bio-solids mixture after HNO_3 digestion

P' = Concentration of PAC after HNO_3 digestion

S' = Concentration of bio-solids after HNO_3 digestion

Now define

where:

A = Fraction of bio-solids remaining after HNO_3 digestion

B = Fraction of PAC remaining after HNO_3 digestion

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and Equation 3 can be rewritten as

$$M' = BP + AS \quad (6)$$

Multiplying Equation 2 by A and subtracting Equation 6 from Equation 2 provides an expression for the PAC concentration in the PAC/bio-sludge mixture

$$P = \frac{AM - M'}{A - B} \quad (1)$$

M and M' are obtained directly by determining the suspended solids concentration before and after acid digestion. Assuming that B is independent of the biosolids concentration and that A is independent of the PAC concentration, A and B can be determined by the acid digestion of the bio-solids and PAC control solutions. Typical ranges for B is 0.9 - 0.95 and A is 0.65 - 0.85.

In order to test the validity of this procedure, known quantities of PAC were added to solutions containing known concentrations of bio-solids. The quantities of PAC added were nominally 500 mg/1, 1500 mg/1, and 3000 mg/1. The difference between the PAC added and the PAC concentration as estimated from the acid digestion procedure was ±13%. Periodically during the course of the study, the validation process was repeated with comparable results.

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APPENDIX C

METRIC CONVERSION FACTORS

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Multiply the U.S. Customary Unit	By	To Obtain
gallons	0.003785	m^3
gpd	4.38×10^{-8}	m^3/sec
gpd/ft^2	0.0407	m^3/m^2 day
gpm	6.31×10^{-5}	m^3/sec
gpm/ft^2	0.0407	m^3/m^2 min
in	2.54	cm
lb	0.4536	kg

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